







**TRANSACTIONS**  
**OF THE**  
**AMERICAN INSTITUTE OF MINING**  
**AND METALLURGICAL ENGINEERS**  
**(INCORPORATED)**

**Vol. 105**

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**IRON AND STEEL DIVISION**  
**1933**

**PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT THE MEETINGS**  
**HELD AT BUFFALO, OCT. 5-6, 1932 AND AT NEW YORK, FEB 20-23, 1933**

**NEW YORK, N. Y.**  
**PUBLISHED BY THE INSTITUTE**  
**AT THE OFFICE OF THE SECRETARY**  
**29 WEST 39TH STREET**



## *Notice*

This volume is the sixth of a series containing papers and discussions presented before the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers since its organization in 1928; one volume each year, as follows:

1928, Iron and Steel Technology in 1928

1929, 1930, 1931, 1932 and 1933, TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Iron and Steel Division

This volume contains papers and discussions presented at the meetings at Buffalo, Oct 5-6, 1932 and at New York, Feb 20-23, 1933

Papers on iron and steel subjects published by the Institute prior to 1928 are to be found in many volumes of the TRANSACTIONS of the Institute; during the past 25 years in Vols. 37 to 45, inclusive; 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive; 73 and 75. Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS may be found by consulting the general indexes to Vols. 1 to 35 (1871-1904), Vols. 36 to 55 (1905-1916), and Vols. 56 to 72 (1917-1925), and the indexes in succeeding volumes.

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PRINTED IN THE UNITED STATES OF AMERICA  
146115

THE MAPLE PRESS COMPANY, YORK, PA.

## FOREWORD

THOUGH this volume of the TRANSACTIONS is not as large as some of its predecessors in the Iron and Steel Division series, it takes second place to none so far as the quality of its contents is concerned. This is saying much; for the Institute in 62 years has enriched the literature of the metallurgy of Iron and Steel as has no other organization in this country. Since its establishment as a semi-autonomous unit, the Division, under the Chairmanship of Sweetser, Waterhouse, MacKenzie, Becket, Speller and Johnston, has maintained professional leadership not only in the science of metals but in the arts of smelting, alloying, and otherwise preparing iron and steel for the user. Membership in the Division—and consequently in the Institute—is a badge of real achievement as a metallurgist; authorship of a paper published in this series of TRANSACTIONS volumes is in itself evidence of attainment beyond the ordinary.

Dr. Johnston, the Chairman of the Division for 1933, and a special committee are engaged in a careful re-examination of the Division's publication program. From this study should result prompter publication and more positive distribution with the maintenance of the highest standard of quality that has always characterized the papers. The Division, it is safe to predict, will continue to carry on as befits the foremost strictly professional organization of iron and steel metallurgists and metallurgical engineers in the United States.

A. B. PARSONS,  
*Secretary.*



# CONTENTS

Foreword	3
Howe Memorial Lecture	6
Institute Officers and Directors	7
Iron and Steel Division Officers and Committees	8

## PAPERS

Steelmaking Processes (Howe Memorial Lecture) By GEORGE B. WATERHOUSE	13
Effect of Variation in Coke Ash on Pig-iron Analysis. By H. W. JOHNSON (With Discussion)	28
Effect of Small Percentages of Chromium on the Quality of Cast Iron By CHARLES O. BURGESS (With Discussion)	37
An Improved Nickel-chromium Hardened Chilled Cast Iron By J. S. VANICK (With Discussion)	53
Properties of Low-carbon Medium-chromium Steels of Air-hardening Type By E. C. WRIGHT and P. W. MUMMA (With Discussion)	77
Hot-hardness of High-speed Steels and Related Alloys By OSCAR E. HARDER and H. A. GROVE (With Discussion)	88
Precipitation-hardening of Copper Steels. By CYRIL STANLEY SMITH and EARL W. PALMER (With Discussion)	133
Oxide Analysis by Iodine Extraction in Steelmaking Problems. By J. J. EGAN, W. CRAFTS and A. B. KINZEL (With Discussion)	169
Analyses of Inclusions in High-carbon Tool Steels. By HAAKON STYRI (With Discussion)	185
Intermediate Phases of the Iron-tungsten System By W. P. SYKES and KENT R. VAN HORN (With Discussion)	198
Studies upon the Widmanstätten Structure, IV.—The Iron-carbon Alloys By ROBERT F. MEHL, CHARLES S. BARRETT and DANA W. SMITH (With discussion)	215
An X-ray Study of Iron-silicon Alloys Containing 0 to 15 Per Cent Silicon. By ERIC R. JETTE and EARL S. GREINER (With Discussion)	259
A Study of the Homogeneity Limits of Wustite (FeO) by X-ray Methods. By ERIC R. JETTE and FRANK FOOTE (With Discussion)	276
A New Thermocouple for the Determination of Temperatures up to at Least 1800°C. By G. R. FITTERER (With Discussion)	290
Index	303

## The Howe Memorial Lecture

THE Howe Memorial Lecture was authorized in April, 1923, in memory of Henry Marion Howe, as an annual address to be delivered by invitation under the auspices of the Institute by an individual of recognized and outstanding attainment in the science and practice of iron and steel metallurgy or metallography, chosen by the Board of Directors upon recommendation of the Iron and Steel Division.

So far, only American metallurgists have been invited to deliver the Howe lecture. It is believed that this lecture would gain in importance and significance were it possible to include metallurgists from other countries, but the Institute has not yet been able to do this on account of lack of special funds to support this lectureship.

The titles of the lectures and the lecturers are as follows:

- 1924 What is Steel? By Albert Sauveur.
- 1925 Austenite and Austenitic Steels. By John A. Mathews
- 1926 Twenty-five Years of Metallography. By William Campbell.
- 1927 Alloy Steels. By Bradley Stoughton.
- 1928 Significance of the Simple Steel Analysis. By Henry D. Hibbard.
- 1929 Studies of Hadfield's Manganese Steel with the High-power Microscope.  
By John Howe Hall.
- 1930 The Future of the American Iron and Steel Industry. By Zay Jeffries
- 1931 On the Art of Metallography. By Francis F. Lucas.
- 1932 On the Rates of Reactions in Solid Steel. By Edgar C. Bain.
- 1933 Steelmaking Processes By George B. Waterhouse.
- 1934 The lecturer will be Frank N. Speller; subject, The Corrosion Problem  
(definite title to be announced later).

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GEORGE B. WATERHOUSE  
*Henry Marston Howe Memorial Lecturer, 1933*

## Steelmaking Processes

BY GEORGE B WATERHOUSE,\* CAMBRIDGE, MASS

(Henry Marion Howe Memorial Lecture†)

It is a great honor to be privileged to give the Howe Memorial Lecture, deeply appreciated because of indebtedness to Professor Howe as a student. During the first of my three years at Columbia University he was absent on sabbatical leave in Europe, but even then kept in touch with my work by correspondence. He was an inspiring teacher and leader, thorough master of his subject, one who demanded great care in experimental work and exacting in regard to correct English in reports and theses. He was equally strict with his own work, and John Howe Hall in a previous Howe Lecture has reported how careful he was in the preparation of his written material. His careful classical training and early environment evidently brought about in him a love of words and their correct use. His attitude and the effect he produced was that of the scientist in search of truth. His interest in his students continued throughout their professional careers and was a constant encouragement and inspiration to them, not ceasing with his death.

The subject today is Steelmaking Processes. It has been chosen for several reasons, including its great importance and Professor Howe's life-long interest in methods of steelmaking. His book on *The Metallurgy of Steel*, published in 1890, was immediately recognized as a most important work, an opinion that has been confirmed as time has passed. About one-third of that book is given to steelmaking processes. Also many of his published papers were on similar subjects, as was pointed out by Professor Sauveur in the first Howe Lecture, and his last published paper in 1922 (the year of his death) was on *Acid Open-hearth Practice*.

It is believed that very few know that his graduating thesis, in 1871, at the Massachusetts Institute of Technology, was on a method of steelmaking. At that time he was twenty-three years old and had entered the Institute two years before after graduating from Harvard. The thesis was carefully written by the young graduate and a reproduction of the title page is given in Fig. 1. It deals with a process of producing steel instead of wrought iron by puddling, a process that attained considerable importance in Europe about 1850 and was introduced in England in 1856. About 1865 it was noticed at a plant in Pennsylvania that when

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\* Professor of Metallurgy, Massachusetts Institute of Technology.

† Presented at the New York Meeting, February, 1933. Tenth Annual Lecture.

the puddling furnaces were lined with Codorus ore the product was steely in nature. The conditions were studied, steel was made at that plant with regularity and introduced to the trade. Attempts were also made to interest other ironmasters in buying and using Codorus ore for the same

*A Thesis on the  
Process of Puddling Steel  
with the  
Codorus Ore  
Presented on Graduating from  
— the —  
Massachusetts Institute of Technology  
by  
Henry Marion Howe, A.B.*

FIG. 1.—TITLE PAGE OF GRADUATING THESIS OF HENRY MARION HOWE, 1871.

purpose. The thesis describes a careful investigation of the method carried out at the Norway Iron Works in South Boston. The Codorus ore was a very siliceous hematite high in potash, and with only a trace of phosphorus. It gave a voluminous slag in the puddling process. It was the same ore mentioned by the great engineer, Alexander Lyman Holley, in an interesting poem. The thesis repays study today. It gives a careful review of the subject in English, French and German literature, including the patents. It describes how the process was carried out at the Norway Iron Works. Systematic samples were taken and analyzed

by the young metallurgist, the chemical methods being given in detail. Fig. 2 shows page 57 of the thesis, from which may be seen the careful way in which the work was recorded and which gives the finished steel analysis in column 6. Such steel was much cheaper than crucible steel,

57

*Results of analyses of iron and slag  
taken at different stages of puddling steel  
by the Cordons process, at Norway Iron Works,  
So Boston Mass (H M Howe)*

	1	2	3	4	5	6
Combined Carbon	<small>graphite 0.15 combined 0.12 total carbon 0.27</small>	3.40	3.25	—	1.10	1.10
Phosphorus	0.16	0.05	0.036	0.03	0.03	0.02
Sulphur	0.004	0.005	0.02	0.007	—	0.002

No 1 Glendon pig iron, No 2

No 2. sample taken 42 min after charge

No 3 " " 57 " " "

No 4 " " 71 " " "

No 5 " " 100 " " "

No 6 Steel bar, product of the operation

*Corresponding analyses of Cinders*

Under taken with	No 2	No 3	No 4	<small>for min before No 5</small>	No 5
Phosphoric acid	2.48	4.91	4.91	3.49	5.20
Sulphur	0.15	0.26	0.24	0.25	0.28
Phosphorus (Corresponding)	0.86	1.07	1.07	1.09	1.08

FIG. 2.—PAGE 57 OF GRADUATING THESIS OF HENRY MARION HOWE, GIVING ANALYSES OF MATERIALS.

it was used extensively for wagon tires, sleigh shoes, toe calks and certain wire products. It was not good for springs.

This thesis, written more than sixty years ago, shows a clear grasp of metallurgical principles; the importance of temperature control is pointed out and the great necessity of proper slag composition. It also points out that there seems to be very little future for puddled steel because of its unreliability and lack of uniformity compared with crucible,

bessemer or open-hearth steel. This opinion has been confirmed by experience because such steel is not made now.

Reference has been made to this early work by Professor Howe because of the evidence given of careful preparation of his subject, correct scientific methods and well drawn conclusions, and above all because of the clear promise of the success that was reached in later years.

In the present discussion it is proposed to cover the steelmaking methods used in the United States, describe them briefly, investigate the trends in regard to tonnage made by the different processes and point out some, at least, of the reasons for those trends.

### CRUCIBLE PROCESS

This old process of steelmaking is simple in principle. Carefully selected charges are melted in crucibles, usually made of fireclay and graphite holding about one hundred pounds. Gas-fired furnaces are generally used. After the charge is melted it is held in the furnace for a period to be freed from excess gases or "killed," as it is termed, then withdrawn and either poured directly into an ingot mold or casting, or else into a ladle where the contents of many crucibles are mixed, after which the steel is poured into ingots or molds. The operation takes from three to five hours. It is an adaptation of the process developed by Huntsman in Sheffield about 1746, which later spread to other countries.

As a rule no additions are made to the original charge, which is melted quietly, killed, then withdrawn and poured. When the process is properly carried out the final material is probably the best steel that can be made. For good practice the charge consists chiefly of high-grade wrought iron, and in Sheffield preference is given to Swedish wrought iron. Very little scrap is used and that only of the highest grade. There is no removal of phosphorus or sulfur and in many cases sulfur increases slightly owing to absorption from the furnace gases, so that raw materials very low in phosphorus and sulfur must be used. Silicon is higher in the finished steel than in the charge, and the superior quality of well made crucible steel is sometimes attributed to this fact. The silicon is reduced from the clay of the crucible walls and enters the steel in an active chemical condition, being, without doubt, one of the helpful factors during the killing process. When it is carefully made crucible steel is very free from nonmetallic impurities and is known as a "clean" steel, the restful quiet conditions which obtain during melting and killing being helpful in this respect.

[The operations of crucible steelmaking as carried out in the Pittsburgh district some years ago were shown by means of slides illustrating charging, melting, pouring from crucibles into a ladle and finally pouring into molds. These slides gave an idea of the care taken in making cruci-

ble steel, the small scale of the operations and the large amount of labor required per ton of steel.]

Fig. 3 shows what has happened to the crucible steel industry in the United States during the last twenty years. The curve does not give the actual tonnage of ingots and castings produced but the percentage of this production compared with the total tonnage. However, at the bottom of this and the other diagrams some tonnage figures have been given.

During this period crucible steel production has steadily declined and has practically disappeared. In 1912 the crucible steel made amounted approximately to 0.4 per cent of the total steel made. It dropped in a fairly regular way and both in 1930 and 1931 was less than 0.01 per cent.

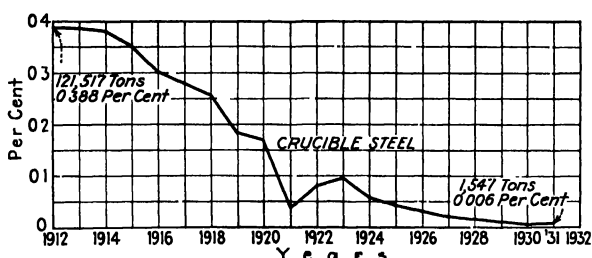


FIG 3 —CRUCIBLE STEEL PRODUCTION IN THE UNITED STATES (PERCENTAGE OF TOTAL TONNAGE).

The steels made by this process are mostly ordinary and special tool steels, special alloy steels and steels for castings. Such steels are needed and used today, so the question naturally arises, Why has the crucible process been practically abandoned in this country? The main reason for this and for the trends in the other processes is undoubtedly economic. Electric-furnace methods have proved to be the sternest and most successful competitors. These methods will be briefly described later. In the first place they have reduced costs by working on a larger scale while still using in general the same raw materials and the same steelmaking practice. Instead of 100-lb. heats the weight has increased, so that for tool steels 1000 lb., one ton, three, six or even ten tons are common. This larger scale operation has naturally greatly reduced the labor costs per ton, overhead and many of the other factors that influence costs. Then as time went on it was found that much cheaper raw materials could be used and that with the increased knowledge of steelmaking the final quality was almost if not quite as good as much of the crucible steel. This again led to striking cost reductions. There is no doubt that in the attempt to meet this hard competition the quality of much crucible steel suffered owing to efforts to use cheaper raw materials,



cheaper and less skilled labor, efforts to increase output and non-attention to the many small details that lead to quality. One of the important requirements of tool steels is uniformity, even if the quality is not of the very highest. If the steels are uniform from one cast to the next, one shipment to another, month after month, year after year, then uniform and good results can be obtained in the machine shops, heat-treating practice can be standardized, time-study results are of value and the shops and factories can rely on the tool steels. European and our older crucible practice met this requirement; methods were the same year after year. Workmen were educated from childhood to carry out practice in the same way that their fathers and grandfathers had done and the final result of many very small factors was good quality and remarkable uniformity in the finished steels. Even this has been recognized by our makers of tool steels by electric-furnace methods, details of practice have been systematized and elaborate tests have been developed which are applied to the finished steel to reveal its "personality" or "timbre" so that uniform material can be supplied for heat treatment and general use.

In regard to castings, the chief merit of the crucible steel was soundness in the finished castings and a rather low initial cost of the steel-making plant. In this field the various competitive factors mentioned above have all played their part, and in addition improved steelmaking practice has shown how sound castings can be made by a number of other and cheaper steelmaking methods such as the acid or basic open-hearth and various electric-furnace methods.

### ACID BESSEMER PROCESS

The first public description of this process was in August, 1856, in a paper published in England by Henry Bessemer. Developments in this country were rapid following 1865. As usually carried out, it is simple in principle. Molten pig iron of the proper composition is poured into the bessemer converter, which is a pear-shaped vessel mounted on trunnions. The converter is placed on its side to receive the charge, which varies in weight from 5 to 30 tons. Air at a pressure of about 20 lb. per square inch enters the converter through numerous holes in the bottom. The air is turned on and the vessel turned upright. The air oxidizes the carbon, manganese and silicon of the charge, the combustion of which together with some of the iron furnishes the heat to carry on the process. The progress of the operation is shown by the flame issuing from the mouth of the converter; this flame is short and dry at first but changes in character as the carbon burns and increases in size. It is a beautiful and characteristic sight. When the carbon is practically all burned the flame drops and the vessel is turned down, after which the blast is shut off. The whole operation or blow takes from 12 to 18 min-

utes. The material is now known as blown metal and contains very little carbon and traces only of silicon and manganese but all the phosphorus and sulfur of the original charge. It also contains considerable oxide of iron, most of which has to be removed to give a product that can be forged or rolled. The usual deoxidizing agent is ferromanganese added to the blown metal while it is being poured into the ladle.

[The operations of bessemer steelmaking practice were illustrated by slides showing a converter, the charging with molten metal, a typical bessemer flame, turning down the converter at the end of the blow and pouring the blown metal into a ladle.]

The result of these operations is bessemer soft steel, used extensively for sheet and tin plate, wire products, pipe and for bar stock. Another important class of bessemer steel is screw stock for free machining purposes, made by adding sulfur to the blown metal together with more ferromanganese than usually. Higher carbon steels can be made by adding the proper amount of molten pig iron to the blown metal together with ferromanganese or by adding the proper amount of a molten mixture of pig iron and a lower manganese alloy called spiegeleisen.

As can be appreciated from this short description, it is very decidedly a tonnage process, large amounts of steel being rapidly and cheaply made from liquid pig iron. It is, however, a process of decided limitations. Liquid pig iron is absolutely essential, so that molten metal is either used direct from the blast furnace, stored in mixers, or cold pig iron must be melted in cupolas. Bessemer ore and bessemer pig iron are well-known terms and allude to the fact that the pig iron cannot contain more than about 0.085 per cent phosphorus, and the ore must not be higher in phosphorus than will give this amount in the pig iron. Then temperature control is a vital necessity of the process, which strictly limits the silicon in the pig iron, which is the main fuel. It is true there is some measure of control of temperature during blowing but not enough to allow very wide limits of silicon. The manganese also of the pig iron cannot be higher than about 0.60 to 0.80 per cent or else a thin and sloppy slag is produced during blowing, which slows down production and leads to increased metallic losses.

Fig. 4 shows, in the lower curve, the trend of the bessemer steel production going into ingots and castings in the United States during the last twenty years. Almost every year has shown a drop in percentage, from 33 per cent in 1912 to 11.6 per cent in 1931. Instead of one-third of our steel being made by this simple and easily carried out process, only a little more than one-tenth is now made. Some of the reasons for this striking decrease may be mentioned.

The reason usually advanced and one that has great weight is in regard to the phosphorus content of the steel. It has increased as the low-phosphorus ores have been exhausted and now runs from about 0.085

to 0.115 per cent and is generally about 0.10 per cent. This has definitely barred bessemer steel from many uses where the carbon of the steel must be fairly high, such as rails, springs, forging steels and even lower carbon steels such as plate and structural steel. In other words, the quality of bessemer steel was not high enough for many engineering purposes and the field was open to the other tonnage process, the basic open hearth. Engineers then acquired the habit of specifying open-hearth instead of bessemer steel for many uses, and bessemer steel suffered accordingly. It is not a "clean" steel as compared with many others, which also bars it from many applications. The use of alloy steels is increasing all the time. Certain alloy steels cannot be made by the bessemer process and many of them that can be made would not have the high quality demanded by consumers and possible of attainment by the basic open-hearth and certain electric-furnace processes.

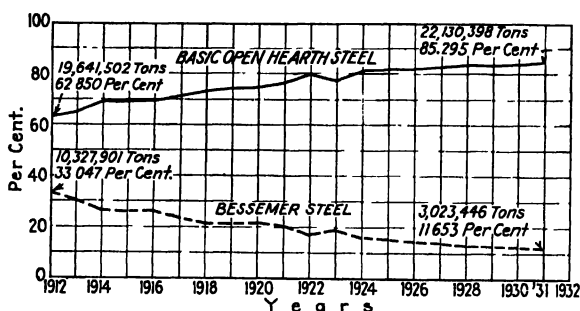


FIG. 4.—BESSEMER AND BASIC OPEN-HEARTH STEEL PRODUCTION IN THE UNITED STATES (PERCENTAGE OF TOTAL TONNAGE).

Another reason is the serious limitation in regard to raw materials. As mentioned before, only a certain kind of pig iron can be used and this must be in the molten condition, a limitation from which the basic open hearth does not suffer. Then the bessemer process can use only a certain percentage of scrap steel, as a rule not over 10 per cent, and this scrap must be in pieces of about 50 to 200 lb. weight. The ability to use any amount and any kind of scrap is a very decided factor in the choice of a steelmaking method; an important subject that will be considered more fully later. Bessemer steel is particularly well fitted for certain products such as pipe, owing to its good welding and machining properties, wire products because of its good drawing qualities, and many sheet products such as tin plate; and the high-sulfur bessemer steels are unexcelled for free machining properties, so that a very large tonnage is used in screw machine products and for bolts and nuts. Even in these fields, however, basic open-hearth steel is a very serious competitor and the main reasons are similar if not quite such good properties and, most decisive of all, equal if not lower costs of production.

## ACID OPEN-HEARTH PROCESS

The open-hearth process developed by Siemens in England and the brothers Martin in France about 1860 was carried out on an acid hearth, so that, like the acid bessemer, the slags produced were acid and there was no removal of phosphorus or sulfur from the charge. This was the first open-hearth process to be introduced and developed in this country and a considerable tonnage of steel is still made by this method. As usually carried out, the furnaces do not exceed 50 or 60 tons capacity and generally run about 20 tons. Carefully selected scrap, low in phosphorus, constitutes the majority of the charge running usually more than 60 per cent, and the rest is equally carefully selected pig iron. The charge is melted and the carbon carefully worked down, the metal being usually tapped into the ladle at about the carbon required in the finished steel.

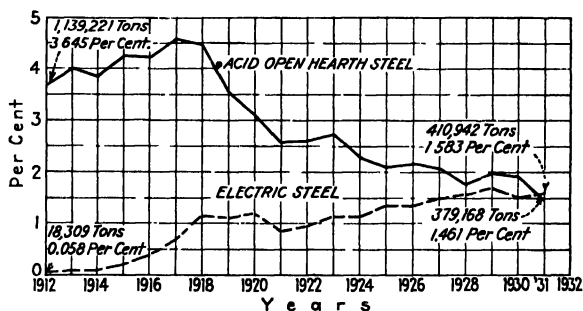


FIG 5.—ELECTRIC AND ACID OPEN-HEARTH STEEL PRODUCTION IN THE UNITED STATES (PERCENTAGE OF TOTAL TONNAGE).

Deoxidizing agents are either added to the metal in the furnace before tapping or partly in the furnace and partly in the ladle. It is a fairly slow process, the time of heats varying from about six to thirteen or more hours, and even after tapping the steel is often held in the ladle for half an hour so that it may be clean and comparatively free from nonmetallic impurities. During the latter part of the process silicon is often reduced from the slag directly into the bath, having an effect similar to that produced in the crucible process. When carefully made the steel is of high quality. About half of the steel produced goes into castings, the remainder going mostly into special products such as forgings for ordinary and ordnance purposes, armor plate, wire products of many kinds including springs, wire rope and bridge cables, special purposes such as razor-blade stock and a whole range of alloy steels.

The percentage production of acid open-hearth steel is shown by the upper curve of Fig. 5. In 1912 it constituted 3.6 per cent of the total production. It rose irregularly during the war years to 4.6 per cent in

1917, when a great deal was used for ordnance purposes, and ever since has sunk, until in 1931 it only amounted to 1.46 per cent. The reasons are not hard to find. It is a fairly high-cost process, because of the selected raw materials that have to be used and the long time needed for melting and refining when making high-grade products. Then it has met very serious competition from the electric-furnace processes and from the basic open hearth. The former can take the same or cheaper raw materials and turn out steels that are equal if not superior in quality. The latter can take much cheaper raw materials and furnish steels for castings and for other purposes that are much lower in cost, and because steelmaking practice has improved and is better understood, the quality in many cases is almost if not quite as good as the acid open hearth.

### BASIC OPEN-HEARTH PROCESS

The use of a furnace lining of basic refractory material was developed by Thomas in England in 1878. It was speedily applied to the bessemer process with great success and is still extensively used in Europe, where the method is called the Thomas process. The first commercial application of the basic hearth to the open-hearth process in this country was in 1888 at the Homestead plant at Munhall, Pa., since when the development has been rapid. It is now the most important steelmaking process in the country and is marked by extreme flexibility in many directions.

The size of the furnaces varies from small capacity, even as low as one ton, to over 400 tons, the average being about 100 tons. The charge may contain no scrap or may consist entirely of scrap. Conversely, 100 per cent or no pig iron may be used. Molten pig iron is generally employed but many plants use cold scrap and cold pig iron. The kinds of fuel used may vary greatly and also the method of carrying out the process, because many modifications have been developed.

The outside appearance of an open-hearth plant is familiar to many, tall chimneys each serving one furnace. The furnaces, each with several working doors, stretch along the inside of the building. The metallic charge usually consists of cold scrap and molten pig iron, a common ratio being 50 to 60 per cent scrap and the balance pig iron. The scrap is loaded by a magnet crane from the scrap pile into charging boxes. These boxes are brought on tracks in front of the furnaces, picked up by a charging machine, projected through an open door into the furnace and emptied on top of the limestone flux that has been already charged. When the scrap is partially melted, liquid pig iron is brought along in a ladle and poured into the furnace through a short spout. The charge is now brought to a liquid condition and carefully worked or refined, numerous tests being taken to judge of the condition of the bath. Finally, when of the proper composition and temperature, it is tapped into a ladle

on the pit side of the furnace, the proper deoxidizers and other additions being made either to the metal in the ladle or usually partly in the furnace and the rest in the ladle.

Like the bessemer flame, the tapping of a heat of steel is a beautiful and impressive sight, especially at night. When the steel is all in the ladle it is raised by the powerful pit crane, carried to the pouring platform and the steel poured into ingots.

[The operations of basic open-hearth practice were illustrated by means of slides showing the exterior and interior of a typical plant, the charging of scrap from a stock pile into boxes, the charging of scrap and of molten pig iron into a furnace, the sampling of the bath, the tapping of the finished steel into the ladle and finally the pouring of ingots.]

The kinds of steel made by this process include almost all the steels made and used with the exception of the tool steels, certain alloy steels such as the stainless steels and the highest grade products for certain forgings, ordnance purposes and particular wire products. The development of this method of steelmaking is shown by the upper curve of Fig. 4. The percentage of the total steel made has steadily and uniformly increased as time has passed. It was about 63 per cent in 1912 and increased almost uniformly to 85 per cent in 1931. Many of the reasons for this consistent growth in production have been indicated in the discussion of the other processes. It is usually carried out on a large scale, so that it is a comparatively low-cost process. It is adapted and applied to the manufacture of a wide range of steels, from those with almost no carbon to those with carbon up to 1.5 per cent, from plain carbon steels to very complex alloy steels. It is capable of turning out steels of high quality by making use of the experience gained over many years.

Two of the greatest factors leading to the development of this process are the wide choice of raw materials and the removal of phosphorus that is brought about during the operation. The charge can run very high in phosphorus, even 1.5 per cent or higher, and yet the finished steel be well within the usual specification limits of not over 0.04 per cent. The importance of this factor has been emphasized by every writer on the basic open-hearth process, because it has made available the enormous supplies of iron ores with phosphorus above the bessemer grade. In regard to removal of phosphorus, this is an elastic process as compared with the crucible, bessemer and acid open-hearth, which are nonelastic.

Not only does this process allow a wide choice in regard to the kinds and amounts of pig iron that may be used but it allows a similar choice in regard to the amounts, conditions and kinds of scrap, and this has become a factor of simply enormous importance because of the great amounts of scrap that have to be used and because of the low cost of scrap during recent years. There is no question that with scrap selling as low as \$3.50 per ton in some cases it is the cheapest raw material in the industry and

the steel plants are simply compelled to adopt the steelmaking method that makes the best use of this cheap raw material.

The importance of the scrap industry and of scrap to the steel industry is not fully realized by many. All steel men know that a great deal of scrap is produced in their own plants. When making steel castings, for instance, it is not unusual for 40 to 60 per cent of the metal poured from the ladle into the molds to be scrapped in the form of heads, risers, gates and sprues, and this percentage is increased a certain amount by the bad castings that are produced even in the best foundries. Then in the rolling mills discards are made from the top and bottom of the ingots when they are rolled, especially from the top where defective material is often found. In certain cases this top discard reaches 35 or 40 per cent. Also, further discards are made in the finishing mills, where billets, blooms, slabs or shapes are rolled to finished sizes. During the preparation of blooms and billets for further rolling, defects are often chipped out with pneumatic chisels, which produces more scrap, and in the finishing mills the final bars or shapes have to be sheared or cut to length, giving crop ends.

The net result is that the final product from the ingot seldom approaches 90 per cent and is often only 70 per cent or lower. One of the greatest possible economies in the steel plants is to increase the percentage of salable product made from the good liquid steel in the ladle, and interesting research work is being carried out along this line. This scrap produced in the steel plants themselves is known as "home" scrap. The remaining scrap used in the steel industry is obtained from many sources. Some of them are spectacular, as when 73 sunken German warships were raised at Scapa Flow, floated to a naval base and cut up for melting scrap, or when Mr. Ford bought 199 ships and used them as a source of scrap for his open-hearth steel plant. Others seem prosaic but are full of romance. The river of scrap starts in many places, such as homes, farms, railroads, machine shops and metal-working factories of all kinds, including automobile plants. It is estimated that 400 lb. of scrap are produced for each automobile manufactured. Some scrap goes direct to the steel plants but the majority goes to centers or yards near the primary steel markets, where it is carefully sorted and classified and when necessary cut by shears or torches or broken into charging-box size. Also, the small material such as sheet and sheet clippings or machine-shop turnings is compressed into bales in hydraulic machines. The Department of Commerce has issued a specification regarding scrap, and no less than 26 classes are recognized for basic open-hearth use. The best known of these is No. 1 heavy melting steel scrap, but No. 2 heavy melting scrap is used considerably and compressed sheet steel is a good third. The first of these is the kind most often quoted in the trade journals and daily newspapers.

The growth of the market or foreign scrap industry has reached large proportions. Various statistics have been brought together by the

Bureau of the Census, by various banks and trade journals and by a body created by the scrap people themselves in 1928 known as the Institute of Scrap Iron and Steel, Inc., with headquarters in New York. Some of these statistics are striking and interesting and will be briefly touched upon. For instance, in 1928 the railroads carried 32 per cent more scrap iron and steel than they did pig iron. In that same year the exports of scrap were over 516,000 tons, and in 1929 they were estimated at 550,000 tons, the largest tonnages going to Japan, Canada, Poland and Italy. Accurate figures regarding scrap consumption were obtained for 1929 and reported in the Biennial Census of Manufactures. In round numbers, 29½ million tons of scrap were used by the steel plants with an estimated value of \$450,000,000. This large tonnage was almost equally divided between home and purchased scrap.

There is an enormous potential amount of scrap in the country, because it is estimated that 750 million tons of steel are in use. Elaborate plans are being worked out for the systematic scrapping and proper use of decrepit or "junk" automobiles by the scrap people and the automobile companies jointly, the scrap dealers having the facilities and trained men for the breaking up of the automobiles, the classification of the scrap and the preparation for the open-hearth furnaces. Much publicity has already been given to the methods proposed or in use in the Detroit and Cleveland districts. Enough has been said to indicate the importance of this industry, which in normal times is estimated to employ 200,000 men, and the importance of this factor in influencing the choice of a steelmaking method cannot be overestimated.

One further factor influencing the growth of the basic open-hearth industry must be briefly mentioned. That is the intensive, ceaseless effort to improve furnace design, operating efficiency and steelmaking practice, not only in this country but all over the world. It is very seldom that a furnace is repaired or rebuilt without some change being made in design. The influence on furnace efficiency over the course of the years has been very great and has led to notable savings in fuel and reductions in cost. Equally effective is the considerable research work being carried out on details of steelmaking practice whereby time is being saved and above all quality is being constantly improved. No such consistent work is being done in regard to the other steelmaking processes except in certain phases of electric-steel practice.

#### ELECTRIC-FURNACE PROCESSES

Electric-furnace processes are of comparatively recent origin but have attained considerable importance. Many types of furnaces are in use and many kinds and modifications of processes. Almost all of them are characterized by the use of a high percentage of scrap in the charge, in many cases 100 per cent.



In some arc furnaces, the charge is melted on an acid hearth and the process closely parallels the acid open-hearth, the steels made being often used for castings. The greater part of electric steel is made in arc furnaces with a basic lining. The process can be carried out to correspond with the basic open-hearth, and similar steels made, but the main advantages of this type of furnace are obtained when a different finishing slag is carried, which means a process different from the basic open-hearth. This slag is higher in bases and can be maintained fluid because of the higher working temperatures of the electric-arc furnace. Also, because of the neutral or slightly reducing atmosphere of the electric furnace, the slag can be deoxidized by means of fine coke or charcoal or ferrosilicon, which with proper procedure leads to a bath free from oxides. This very basic fluid slag has an affinity for sulfur and with good practice the bath can be made very free from sulfur, so that when the process is used to full advantage pure clean steels can be made, superior to basic open-hearth steel and possibly equal in quality to any steels that are made.

Electric-arc furnaces vary in capacity from about 100 lb. to 90 tons, the 3, 6 and 10-ton furnaces being popular sizes. The steels made are of every class, mostly of high-grade type such as tool steels, forging and special-purpose steels, alloy tool steels such as high-speed steel and all the grades of alloy steels including the stainless steels. In making alloy steels the ferroalloys can be added to the deoxidized bath with very little loss of the alloying elements, which is important from the cost standpoint when dealing with expensive alloys.

A very interesting recent development of electric-furnace practice has been the high-frequency or coreless induction furnace. The principle of this furnace is simple. High-frequency current, usually at 960 cycles, is sent through a water-cooled copper coil. This induces current in the metal contained in the crucible surrounded by the coil and speedily brings it to a molten condition. The crucible can be lined with acid, neutral or basic material. It is claimed that refining by suitable slags can be carried out but as a rule the process is simply that of melting, closely corresponding with the old crucible process. This modern electric crucible process is already of considerable importance. The furnaces vary from a few pounds or even ounces in capacity to over four tons. All grades of ordinary and special tool steels are made, and alloy steels, and the furnace has been very successful in remelting stainless-steel scrap.

[Slides were shown of induction crucible furnaces including a drawing to illustrate the principle of the furnace. These slides included an installation with two 600-lb. furnaces, another with two 1000-lb. furnaces, another with two similar furnaces, one with a battery of four 600-lb. furnaces for making tool and alloy steels, which was a particularly good example of a well laid out and clean plant, and finally a slide showing the pouring of a large furnace which melts and prepares 4 tons of stainless-steel scrap in from 2 to 2½ hours.]

The growth of the electric-steel production is shown in the lower curve of Fig. 5, which shows a bulge during and shortly after the war years and steady growth since that time, the production being only 0.06 per cent in 1912 and having risen to 1.6 per cent in 1931.

Some of the reasons for this growth may be given, but many have been mentioned already under the discussion of the other processes. High-grade steels can be made by various modifications of the electric-furnace process and at considerably cheaper cost than by the crucible process. Heat produced from electric power can be easily controlled and whenever the cost of power is low enough the steel competes in cost with acid open-hearth and in some cases with the better grades of basic open-hearth steel. Cheap raw materials can be successfully used in many cases, which again leads to lower costs, and, as mentioned before, the electric-furnace processes are most successful for the production of many of the alloy steels. More and more alloy steels are being used each year, the percentage compared with the total steel rising from 2.5 per cent in 1912 to 5.6 per cent in 1931, so that here is a very important factor leading to the increase of electric-steel production.

### CONCLUSION

In reviewing, as has been done, the trend of the steelmaking processes during the last twenty years, there is a great temptation to forecast what will happen during the next twenty years. It would be easy and instructive to extend the curves that have been shown and predict the percentages of the total steel that will be made by the various processes. There is no escaping the conclusion that the basic open-hearth process will continue to grow. It is such a marvelous process, so flexible in many ways, suited to so many varying raw materials and final requirements that mankind will continue to make increasing use of it. It would also seem that the production of electric steel would continue to increase. The main factor of cost, that of the electric power used, shows promise of decreasing in the future. Also, electric furnaces are comparatively new and subject to improvement, and the induction furnaces offer much promise in regard to melting under controlled atmospheres or even under a vacuum with results that cannot be accurately predicted.

The end is not yet in regard to the steelmaking processes of the future, changes have been rapid even during such a short space of time as twenty years, and the younger men in the audience can look forward to many problems for them to face and solve as the years come.

May I request that a moment of silence be observed at the conclusion of the Tenth Howe Memorial Lecture in honor of Professor Henry Marion Howe.

[As mentioned in the text, slides were shown during the lecture, numbering 34 in all, which are not reproduced.]

## Effect of Variations in Coke Ash on Pig-iron Analyses

BY H. W. JOHNSON,\* INDIANA HARBOR, IND.

(New York Meeting, February, 1933)

DURING part of the year 1932, conditions at the plant of the Inland Steel Co. made possible the collection of data on two of the variables of blast-furnace operation, between which we observed an interesting correlation. The variation in percentage of coke ash in the coke seemed to be reflected in the variations in percentage of silicon and sulfur present in the iron.

This subject is of particular interest during this period of low production because of its effect on quality and cost of pig iron. The consumers of pig iron are now more exacting in their requirements. Formerly 0.050 per cent sulfur was considered satisfactory; now many foundries and steel plants insist on iron under 0.030 per cent sulfur and expect it to average 0.025 per cent sulfur. To attempt to produce iron so low in sulfur and still have reasonably good furnace operation means that everything possible must be done to minimize all variations.

This subject is also directly connected with the cost of producing iron. A blast furnace operates most economically and efficiently in rather narrow limits and so any variable that has range enough to disturb regular operation must be moderated. The importance of regularity is accepted and the methods followed to eliminate variations in materials such as coke and iron ore are recognized as indispensable.

### UNIFORMITY OF ORE AND VARIATIONS IN COKE ASH

The delivering of uniform cargoes of well mixed ore to the blast furnace involves much handling and expense, but it is accepted that the trouble and expenditure are justified. After the ore reaches the dock, further mixing is assured by spreading ore in thin layers, preventing segregation by keeping piles level, variations in digging, and the use of several bins for one ore. And finally, the fact that the furnace burden generally contains three or more ores, together with several miscellaneous materials, eliminates the possibility of ill effects due to variations in any one. Thus, much effort is made to insure a uniform ore.

But a variation in the percentage of silicon in ore is less detrimental than a variation in the percentage of ash in coke. The former affects

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\*Superintendent of Blast Furnaces, Inland Steel Co.

primarily the acidity of the slag only, the latter both the acidity of the slag and the heat available.

A variation in the percentage of ash in coke is detrimental for two reasons: it varies the fixed carbon available for smelting and it varies the acidity of the slag. An increase of 1 per cent in the ash generally decreases the fixed carbon in the coke 1 per cent, and therefore decreases the temperature of the hearth, with consequent increase of the sulfur in the iron. It also increases the material to be smelted, with additional decrease in temperature and increase in sulfur.

The change in analysis of the slag produced has an additional effect. Ash is composed primarily of silica and alumina, therefore any increase of 1 per cent means that approximately twice that amount of stone ought to be added to keep the ratio of acids to bases constant and to prevent the increased acidity from causing an increase in silicon (in spite of the decrease in temperature) and a further increase in sulfur.

In normal operation the burden and stone will be regulated closely enough to make distinctly noticeable a variation of 500 lb. of ore or 150 lb. of stone. Then if the coke ash increases 1 per cent, 100 lb. of fixed carbon are replaced, the equivalent of 250 lb. of ore. The 100 lb. of additional slag produced require about 25 lb. of coke, which are equivalent to 62 lb. of ore, or a total of 312 lb.

The effect of slag analyses is also significant. Normally the stone required to keep the slag of the proper basicity is regulated by increasing or decreasing the amount charged by 150 lb. Then if the ash increases 1 per cent, there are 100 lb. of additional acids to be fluxed, which require 200 lb. of stone; that is, more than the accepted limits. This increased acidity causes the silicon and sulfur in the iron to increase.

Of course changes as large as these have obvious effects. The following data were collected in an effort to show that even smaller variations than these have noticeable effects on the furnace and are reflected in the analysis of the iron produced.

#### FURNACES AND OPERATION

During the period under discussion two furnaces were in operation. No. 2 furnace has a 19-ft. hearth, 88 ft. 3 in. from tapping hole to deck ring, and has produced 1,100,000 tons of iron of various grades, mostly basic iron. The practice of this furnace during the months under discussion is shown in Table 1.

No. 4 furnace is 20 ft. in the hearth, 94 ft. from tapping hole to deck ring, and has produced 370,000 tons, all of which has been basic iron. This furnace is equipped with a coke-screening arrangement in the stock house while No. 2 has none, which accounts for much of the lower coke consumption. The practice on this furnace during the period is shown in Table 2.

TABLE 1.—*Practice of Furnace No. 2*

1932	Tons	Coke Rate	Average Blast Temperature, Deg C	Average Iron Analysis		Sinter, Per Cent	Quality, Per Cent	Iron over 0 040 S, Per Cent	Wind Cu Ft per Min
				Si	S				
June	344	1596	1458	1 08	0 031	8 32	98 1		21,000
July	255	1597	1342	1 17	0 029	5 68	91 3		21,000
Aug	252	1607	1374	1 17	0 028	3 97	97 2	1 0	21,000
Sept	248	1687	1438	1 12	0 029	2 92	95 9		21,000
Oct	250	1634	1387	1 15	0 026	4 71	97 9		21,000

During normal times, these furnaces are operated on 50,000 to 55,000 cu. ft. of wind per minute. In July, 1931, owing to decrease in demand for iron, it was necessary to decrease the wind, and this slow rate of operation has been continued to date. The distinct drop in tonnage on No. 2 furnace was caused by the fact that early in July it was found

TABLE 2.—*Practice of Furnace No. 4*

1932	Tons	Coke Rate	Average Blast Temperature, Deg C	Average Iron Analysis		Sinter, Per Cent	Quality, Per Cent	Iron over 0 040 S, Per Cent	Wind, Cu Ft per Min
				Si	S				
June	495	1523	1372	1 07	0 029	14 83	97 2		31,000
July	503	1504	1315	1 10	0 028	8 72	98 2		31,000
Aug	515	1480	1292	1 13	0 028	7 50	97 3		31,000
Sept	520	1501	1332	1 10	0 026	3 76	97 5		31,000
Oct	510	1518	1303	1 10	0 026	5 12	98 5		31,000

desirable to further decrease tonnage, therefore the furnace was fanned 7 hr. every night. This practice was continued during the remainder of the period.

Both furnaces operated smoothly during the period of observation. The coke was of excellent quality and very consistent. It was not necessary to reduce or increase the burden more than a reasonable amount, on account of a cold or hot furnace. Without coke of such uniformly high quality, we would have been unable to trace the very slight variations under discussion.

#### SAMPLING OF COKE

It is rather difficult to secure a representative sample of a large volume of coke, consequently any conclusion arrived at that is based on sampling may be questioned. However, I believe that at Inland we have a good arrangement and that the samples are representative. Coke is conveyed from the ovens to a bin on the blast-furnace high line by belt. At the

discharge end of the belt is a bucket as wide as the belt, mounted on a shaft. At regular intervals an operator turns the handle that cuts a section of the stream. The bulk aggregate for each 8-hr. shift is collected, crushed to uniform size and quartered to the usual size for laboratory sample.

We feel that the sampling is accurate because we have been able to plot changes in total burden with changes in coke ash. Fig. 1 shows such a correlation during a 22-day period in January and February, 1931.

### PREPARATION OF DATA

In our early studies, charts were drawn of coke-ash and iron analyses and attempts were made to correlate the two. This was not successful. Since it was the variation in the coke ash that was of interest, when this

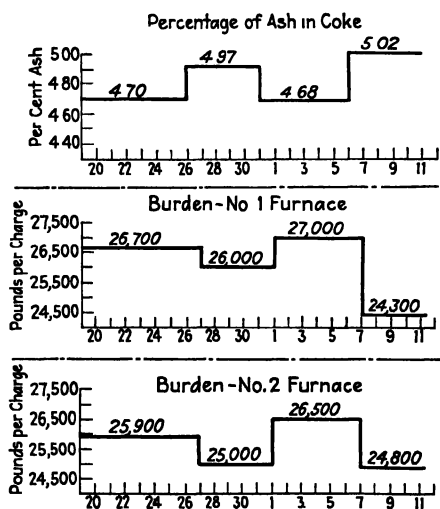


FIG. 1.—VARIATIONS IN TOTAL BURDEN AND VARIATIONS IN THE PERCENTAGE OF COKE ASH, JAN. 20 TO FEB. 11, 1931.

was plotted directly the changes were more obvious, therefore the procedure outlined below was followed.

If the coke ash for the 12 to 8 turn of one day was 5.00 per cent and for the 8 to 4 turn was 4.50 per cent, there was a difference of 0.50 per cent, or 50 points. Then if the ash on the 4 to 12 turn was 4.30 per cent there was a difference of 0.20 per cent, or 20 points. This difference in ash for each of the succeeding turns was determined for the entire period of 5½ months and the data were plotted as shown on Fig. 2. Then the chart was examined and the periods of high and low variation were chosen as shown.

The variations in silicon and sulfur were determined in the same manner (Fig. 3). If the analysis of one cast was 1.05 per cent silicon

and 0.027 per cent sulfur, and the following cast was 1.15 per cent silicon and 0.025 per cent sulfur, there was a difference of 0.10 per cent in the

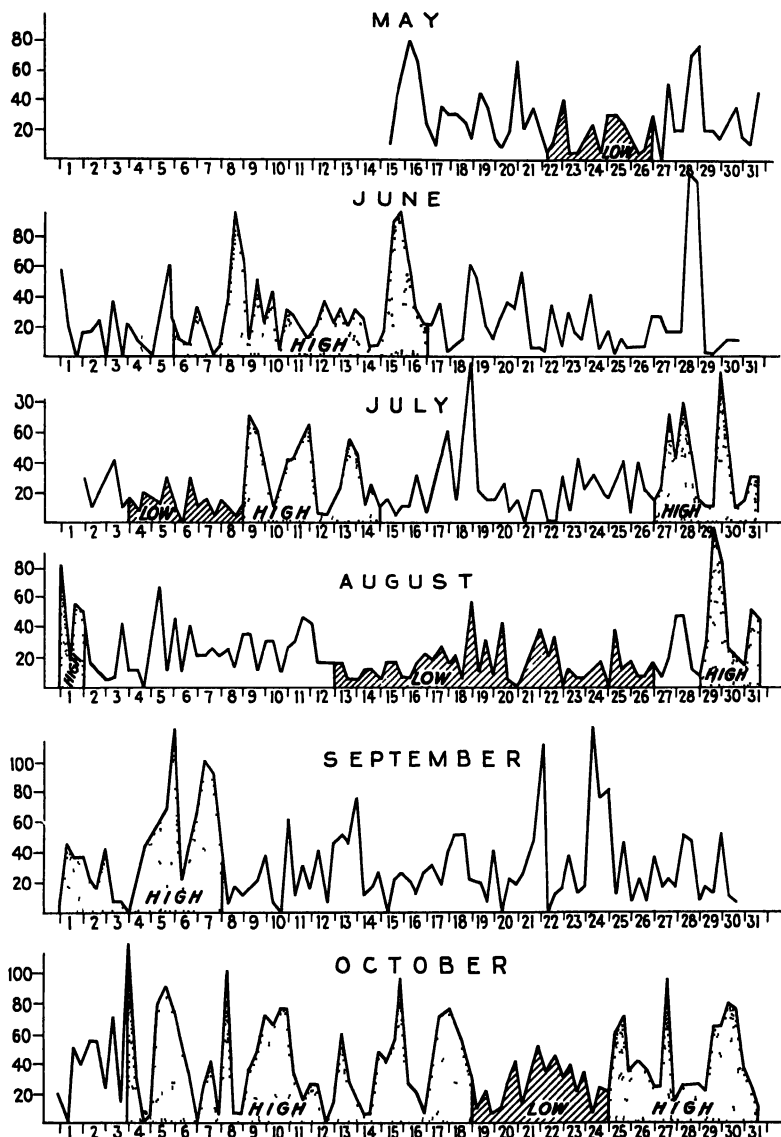


FIG. 2.—VARIATIONS IN COKE ASH FOR EACH EIGHT-HOUR TURN, MAY 16 TO OCT 30, 1932.

silicon and 0.002 per cent in the sulfur, or 10 and 2 points of variation respectively. The variations for both silicon and sulfur for each cast were then totaled and averaged for each period. Due allowance was

made for the interval between the time the coke was sampled and the time that coke reached the tuyeres. See Table 3.

There might possibly be two occasions when the variation in coke ash would be the same but the effect on the furnace would be different. For instance, five consecutive analyses in one case might show 5.50, 5.00, 5.50, 5.00, 5.50 per cent ash while another case might show 5.50, 5.00,

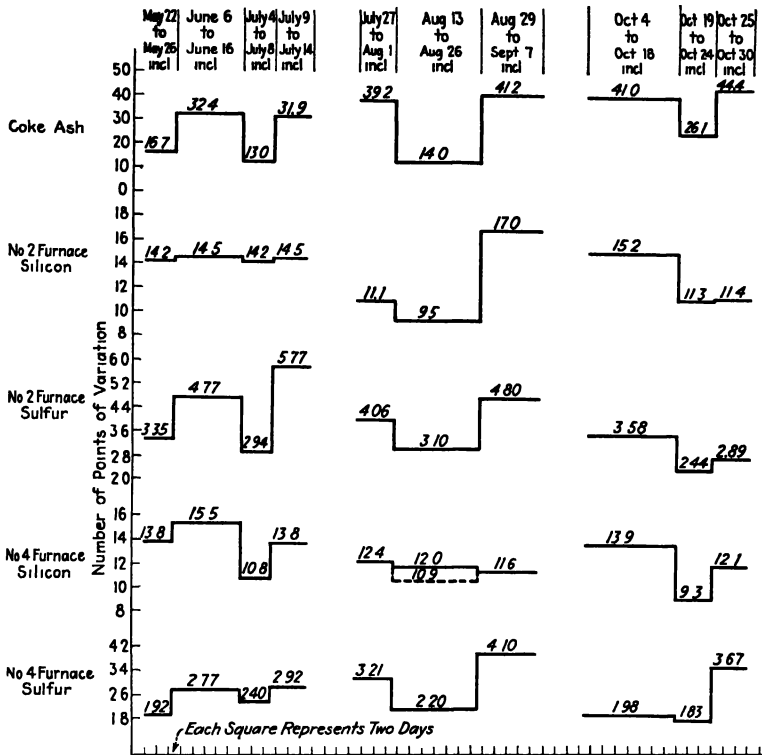


FIG 3.—AVERAGE VARIATION OF SILICON AND SULFUR IN IRON DURING PERIODS OF HIGH AND LOW VARIATION IN COKE ASH.

4.50, 4.00, 3.50 per cent. When the variations in these two cases were plotted, they would look the same, although one might have no detrimental effect while the other one would. This possibility was disregarded entirely, to avoid complications.

### CONCLUSIONS FROM CURVES

From an examination of the curves, it is probably fair to conclude that there is a relationship between variations in coke ash and variations in silicon and sulfur in the iron. It would be more conclusive if the variations in the coke ash over a longer period of time had been plotted and more periods had been studied. However, the fact that the rela-



TABLE 3.—Average Variations for Each Month and for Periods Studied

Month	Coke Ash		No 2 Furnace				No 4 Furnace			
	Actual Average, Per Cent	Average Variation, Per Cent	Average Si, Per Cent	Average S, Per Cent	Variations, Per Cent		Average Si, Per Cent	Average S, Per Cent	Variations, Per Cent	
					Si	S			Si	S
May	4 20	25 9	1 15	0 028	16 5	3 08	1 12	0 026	13 6	2 76
June	4 17	25 2	1 08	0 031	14 6	4 06	1 07	0 029	15 6	3 10
July	4 03	25 1	1 17	0 029	15 0	4 55	1 10	0 028	12 3	2 70
August	4 06	27 0	1 17	0 028	11 9	3 71	1 13	0 028	12 5	2 40
Sept.	4 95	30 3	1 12	0 029	14 8	4 01	1 10	0 028	11 2	3 20
Oct	5 14	37 8	1 15	0 026	14 4	3 30	1 10	0 026	12 9	2 30

## VARIATIONS FOR PERIODS STUDIED

Period, Inclusive	Type	4 19	16 7	1 13	0 029	14 2	3 35	1 09	0 026	13 8
5/22 to 5/26 6/6 to 6/16 7/4 to 7/8 7/27 to 8/1 8/13 to 8/26	Low	4 19	16 7	1 13	0 029	14 2	3 35	1 09	0 026	13 8
	High	4 21	32 4	1 09	0 032	14 5	4 77	1 09	0 027	15 5
	Low	3 98	13 0	1 19	0 029	14 2	2 94	1 07	0 027	10 8
	High	4 16	39 2	1.08	0 028	11 1	4 06	1 15	0 030	12 4
	Low	3 94	14 0	1 21	0 028	9 5	3 10	1 13	0 027	12 0
8/29 to 9/7 10/4 to 10/18 10/19 to 10/24 10/25 to 10/30	High	4 68	41 2	1 11	0 032	17 0	4 80	1 13	0 031	(10 9)
	High	5 10	41 0	1 15	0 027	15 2	3 58	1 10	0 026	13 9
	Low	4 89	26 1	1 15	0 024	11 3	2 44	1 10	0 027	9 3
	High	5 28	44 4	1 13	0 027	11 4	2 89	1 05	0 029	12 1

tionship was evident on two furnaces simultaneously is perhaps more conclusive than if it should repeat on one furnace many times.

The line showing the low period in August on No. 4 furnace represents an average variation in silicon between successive casts of 12 points. In the latter part of this period there was one day when the furnace was obviously overburdened, with a corresponding drop in silicon. A decrease in burden and a too generous increase in blast temperature caused the silicon to increase rapidly. This excessive variation was due to the operators, and not to coke ash. If this day is excluded the average silicon variation would be 10.9, as shown by the dotted line (Fig. 3).

It is noticeable that during the low period in October the coke ash variation of 26.1 points is much higher than in other low periods, although the variations in silicon and sulfur are not. This was due to the fact that the furnace was more basic at that time. It was found desirable in the latter part of September to furnish the open hearth with iron lower in sulfur than before. This increase in lime had a similar effect on the silicon variations.

The most conclusive comparisons are those that occur in adjacent periods, as in the last three indicated. It was during these periods that the excessive swings in the iron analyses were noted and this study was made. In comparing adjacent short periods, many variables are eliminated that would be introduced in a comparison of long periods. For instance, it would be unfair to compare the month of October with the month of August, because the furnaces were more basic during the latter month and this increased basicity might have more effect on silicon and sulfur variations than would any difference in variation of coke ash.

There is a possibility that the physical characteristics of the coke used during the period may have had some influence on the furnaces and consequently on the iron analyses. It is known that the agglutinating properties of coal often differ greatly in a restricted area of the same coal seam, sometimes even in the same mine. However, it is probable that in this case this influence can be disregarded because of the nature of the coals used. The low-volatile coal came from two mines that had been selected from a dozen mines in the same area after extensive sampling and testing. The high-volatile coal came from our own mine, which has been thoroughly sampled and analyzed without finding evidence of any marked difference in coking qualities in any part of the mine.

Furthermore, during this period there were no changes in coking time and only very slight changes in the percentages of low-volatile and high-volatile coals used in the mixture to the ovens.

Therefore we feel that neither the variations in the coking quality of the coal itself, the mixtures of coal used or the process of manufacture had any marked influence on the furnace. We believe that there is a correlation between the variations in percentage of ash and variations

in iron analyses. These variations are due to the effect that change in percentage of coke ash has on the slag in the furnace, and likewise to the effect that change in the amount of fixed carbon in the coke has on the temperature of the hearth.

### SUMMARY

The variations in the coke ash for a period of 5½ months have been plotted, and periods have been chosen in which there was either considerable or little variation in coke ash. The average variation for each succeeding cast of the silicon and sulfur was calculated for each period and a rather definite correlation was noted.

Maximum blast-furnace efficiency is attained when variations are at a minimum. The correlation shows that these variations noticeably reduce the efficiency. It is certain that the expenditure of a reasonable amount of money to insure still further mixing of coals and attain still more uniform coke would be economical.

### DISCUSSION

R. P. HUDSON, Wayland, Ky. (written discussion).—The author has written what is probably a pioneer paper on the subject of the effect of variations in the percentage of ash in the fuel on the analysis of the pig iron. Within the past few years several papers have attempted to show the effect of variations in the percentage of coke ash on fuel consumption. Mr. Johnson has treated the matter from a somewhat different angle and has presented some valuable and informative data.

Mr. Johnson realizes the difficulty in securing a representative sample of a large volume of coke. However, the sampling of the coke at Mr. Johnson's plant, as described by him, is certainly good practice and the method should yield results that are accurate within ordinary commercial limits.

The real value of Mr. Johnson's paper consists of the presentation of actual blast-furnace data. These data have been correlated with the variations in pig-iron analyses, due to variations in coke ash, from the theoretical point of view. A good agreement between theory and practice has been shown.

One interesting feature of the author's paper is the data showing the fuel consumption using low-ash coke. The fuel rate is low, although the furnace is blown with less than half the usual amount of wind. This is another illustration of the value of low-ash coking coals.

Mr. Johnson remarks that there is a possibility that the physical characteristics of the coke used during the period may have some influence on the furnaces and consequently on the iron analyses. However, there is nothing in his data to indicate that there was any change in the physical properties of the coke, although there was an extreme variation of 1.34 per cent ash in the coke. This variation in ash percentage was undoubtedly due to a variation in the extraneous ash in the coking-coal mixture.

I believe Mr. Johnson's conclusion, that the coking quality of the coal mixture has but little influence on the furnace, is correct. There is undoubtedly a correlation between the variation in the percentage of ash and variations in the analyses of the pig iron. There is considerable evidence to show that these variations are entirely due to the change in the composition of the slag and changes in hearth temperature, due to variations in the percentage of fixed carbon in the coke.

# Effect of Small Percentages of Chromium on the Quality of Cast Iron

BY CHARLES O. BURGESS,\* NEW YORK, N. Y.

(Buffalo Meeting, October, 1932)

THE improvement in the quality of cast iron by means of alloy additions has been a metallurgical accomplishment of recent years. Work in this field has shown that chromium is one of the most effective of such additions but, in general, the influence of chromium has been studied only in connection with other alloying additions, with irons other than foundry irons, or with relatively high percentages of chromium. The present study was initiated for the purpose of determining the influence of small additions of chromium (0.25 to 1.00 per cent) on the quality and resultant properties of cast irons of various foundry grades. The effect of small chromium additions on cast iron was investigated with particular reference to casting characteristics, hardness vs. section, strength, machinability, heat resistance and structure.

## MATERIAL TESTED

Three separate types of cast iron were investigated as to the effect of small chromium additions. The first series of these irons was prepared from remelted foundry cast iron at the Union Carbide and Carbon Research Laboratories, and the other two series consisted of cupola melts made under usual operating conditions.

The first series was made by melting 30-lb. charges of foundry scrap iron containing 2.86 per cent carbon, 2.72 silicon, 0.50 manganese, 0.062 sulfur and 0.794 phosphorus in a carbon resistance furnace. The chromium was added as high-carbon ferrochrome just before pouring. The irons were cast at approximately 1250° C. (2282° F.). The analysis and physical properties of these irons are given in Table 1, test 1. The second set of cast irons was made in a cupola in accordance with normal practice, the charge containing approximately 42 per cent steel scrap and the chromium additions being made to the ladle. Analysis and tests of these heats are shown in Table 1, test 2. A small amount of copper was present in heat C of this series.

Further data on the effect of chromium on strength were obtained from a third series of 13 cupola heats containing from 0.06 to 0.50 per cent chromium and made without steel additions. The heats were all

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\* Union Carbide and Carbon Research Laboratories, Inc.

within the analysis limits 3.60 to 3.92 per cent carbon, 2.00 to 2.50 per cent silicon, 0.50 to 0.63 per cent manganese, 0.042 to 0.080 per cent sulfur, and 0.300 to 0.485 per cent phosphorus. Ladle additions of chromium were made in the form of high-carbon ferrochrome.

TABLE 1.—*Analyses and Physical Properties of Cast Irons*

Sample No	Composition, Per Cent							Physical Properties of 1½-in Bar 12-in Centers			
	Total C	Comb C	Si	Mn	Cr	P	S	Transverse Strength, Lb	Deflection, In	Tensile Strength, Lb per Sq In	Brinell Hardness
TEST 1											
1-A	2.80	0.33	2.28	0.50	0.03	0.078	0.081	2,300*	0.12	25,200	152
2-A	2.78	0.41	2.42	0.50	0.26			2,900	0.15	29,600	176
3-A	2.83	0.63	2.80	0.50	0.37			2,800	0.14	30,600	185
4-A	2.93	0.83	2.22	0.50	0.52			2,800	0.11	29,200	192
TEST 2											
A	2.80	0.46	2.53	0.77	0.01	0.240	0.092	3,500 <sup>b</sup>	0.103	36,270 <sup>b</sup>	200
B	2.85	0.52	2.52	0.70	0.48			4,035	0.112	42,550	212
C	2.98	0.57	2.57	0.80	0.79			3,750	0.103	41,650	217

\* Average of two tests    <sup>b</sup> Average of three tests.

The recovery of chromium from ladle additions was found to be approximately 90 per cent in these tests. While ladle additions of chromium were made throughout the series, an alternate method of addition is available—that of adding briquetted chromium to the cupola charge.

The influence of small chromium additions was further checked in a number of remelt heats made in a high-frequency furnace. Although these heats differ somewhat from those likely to be encountered in foundry practice, they are confirmatory as regards the effect of chromium on the strength, and are listed in Table 2.

TABLE 2.—*Effect of Chromium in Remelt Heats*

Sample No.	Composition, Per Cent						Physical Properties of 1½-in. Bar, 12-in Centers			
	Cr Added	Total C	Comb. C	Cr	Si	Mn	Transverse Strength, Lb.	Deflection, In.	Tensile Strength, Lb per Sq In.	
1-C	Nil	2.48	0.40	Nil	2.35	0.52	2,550	0.083	28,975	
10-C	0.50	2.38	0.46	0.46	2.60		3,350	0.095	40,050	
2-C	1.00	2.56	1.58	1.01	2.39		3,700	0.090	41,925	
1-D	Nil	2.77		Nil	2.25		2,200	0.12		
2-D	0.64	2.67		0.63	2.25		2,675	0.11		

As representative of comparative results obtained by other investigators, the results reported by Shipley<sup>1</sup> on a series of cast irons containing varying amounts of chromium are shown in some of the curves (Figs. 1 and 3). The total carbon content of these cast irons was 3.32 to 3.45 per cent; silicon, 2.05 to 2.11; manganese, 0.60 to 0.63 and nickel, 0.41 to 0.53; while the chromium content varied as shown in the curves from 0.14 to 0.37 per cent. The mix was reported as consisting of approximately 50 per cent return scrap and 15 per cent steel.

The cast irons listed above, containing steel additions varying from nil to 42 per cent, with carbon, silicon, manganese, phosphorus and sulfur as reported, are considered to be representative of cast irons usually encountered in the foundry.

### CASTING CHARACTERISTICS

To determine the influence of chromium on fluidity, cupola cast irons containing various amounts of chromium up to 0.9 per cent were used to cast transverse bars, fittings, 2-in. elbows and plates. No appreciable difference in the fluidity of the cast irons was noted in these sections. However, other work has shown that in pouring castings having very restricted or thin sections it may be advisable, as with pearlitic iron, to pour the metal hotter than in the case of ordinary gray iron.

A number of cylindrical castings 2½ in. in diameter were sectioned to determine porosity. It was noted that the presence of 0.50 per cent chromium resulted in a distinct decrease in porosity. No measurements of the relative density were made in the present series of tests, but other investigators have reported that small additions of chromium refine the grain and increase the density of cast iron.

### HARDNESS OF CAST IRON AS INFLUENCED BY CHROMIUM ADDITIONS AND EFFECT OF SECTION

As indicated in Table 1, the effect of chromium is gradually to increase the hardness when the iron is cast in standard arbitration bars, 1.20 in. in diameter. This change in hardness as influenced by chromium content is shown in Fig. 1. It is apparent from these curves that given a cast-iron base with a hardness of 145 to 165, the addition of chromium increases the hardness progressively until, with 0.50 per cent chromium present, it is about 190 to 200 Brinell. For purpose of calculation, it may be assumed that each 0.10 per cent of chromium in this type of iron causes a rise in hardness of approximately 8 to 10 points Brinell.

When a cast iron has an original hardness around 200 Brinell the relative increase in hardness on the addition of small amounts of chromium is apparently much less marked. This can be seen in the cast

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<sup>1</sup> See bibliography at end of paper.

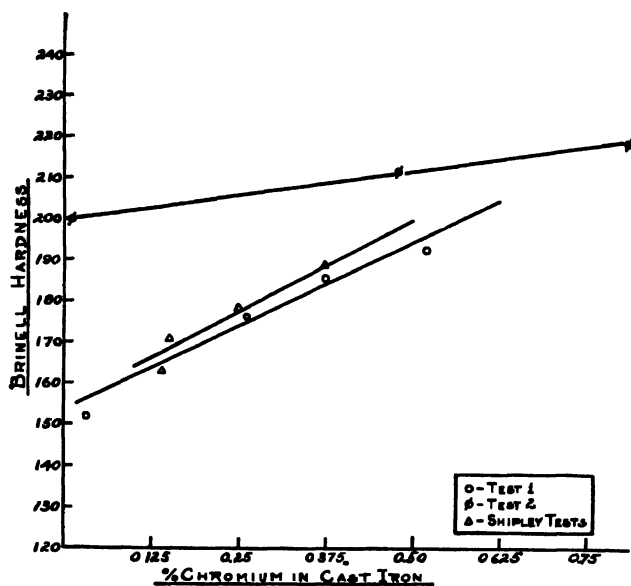


FIG. 1.—EFFECT OF CHROMIUM ON HARDNESS.

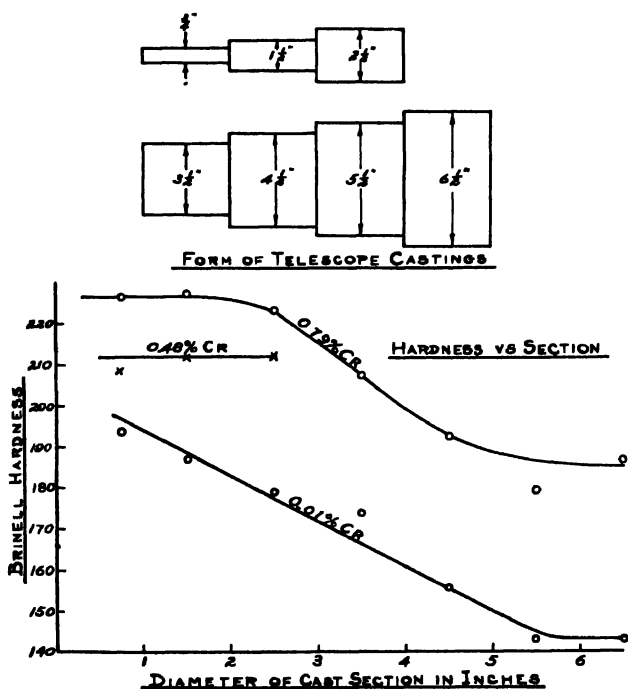


FIG. 2.—EFFECT OF CHROMIUM ON HARDNESS VERSUS SECTION.

irons of test 2. This same modified hardening effect of chromium on cast irons of originally high hardness can be traced in the investigations of Donaldson and Trantin<sup>2</sup>, who record an increase in hardness of only 10 to 27 points Brinell on the addition of 0.50 per cent chromium to cast irons with an original hardness of 223 and 207 respectively.

To test the influence of section on the relative hardness of plain and chromium-treated cast iron, telescope castings were made from the

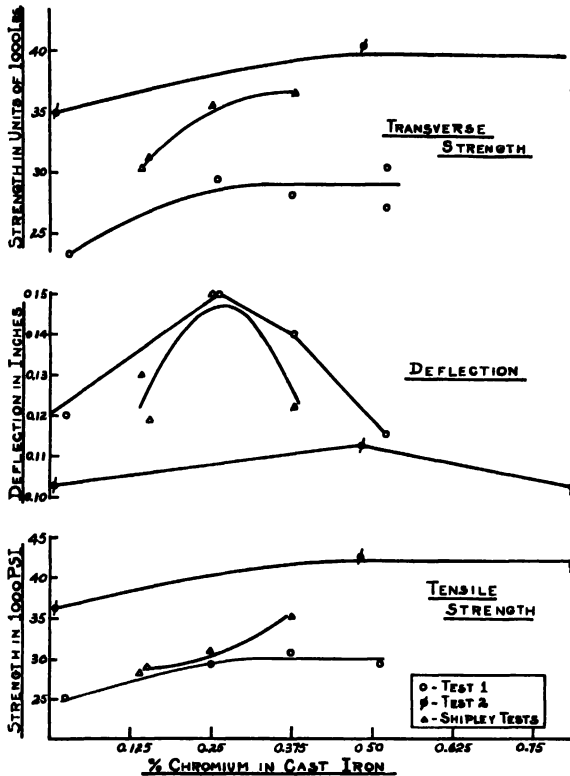


FIG 3.—EFFECT OF CHROMIUM ON PHYSICAL PROPERTIES

three irons shown in Table 1, test 2. These irons contain no (0.01 per cent) chromium, 0.48 per cent chromium and 0.79 per cent chromium respectively. The form of these castings and the results of hardness tests on sections of different thicknesses are shown in Fig. 2. Sections larger than  $2\frac{1}{2}$  in. in diameter were cast only of the irons containing no chromium and 0.79 per cent chromium. The presence of only 0.48 per cent chromium is sufficient entirely to prevent softening on an increase of section from  $\frac{3}{4}$  to  $2\frac{1}{2}$  in. With 0.79 per cent chromium present the

<sup>2</sup> See bibliography at end of paper.



hardness of a 6½-in. section does not fall below approximately 180 Brinell, as compared to a drop in hardness to 143 Brinell in the iron receiving no chromium addition.

It is apparent from this survey that a small addition of chromium is effective in preventing excessive softening of the cast iron in heavy sections.

### STRENGTH OF CAST IRON AS AFFECTED BY CHROMIUM ADDITIONS

The curves in Fig. 3 illustrate the effect of small additions of chromium on the strength and the deflection of the cast irons listed in Table 1.

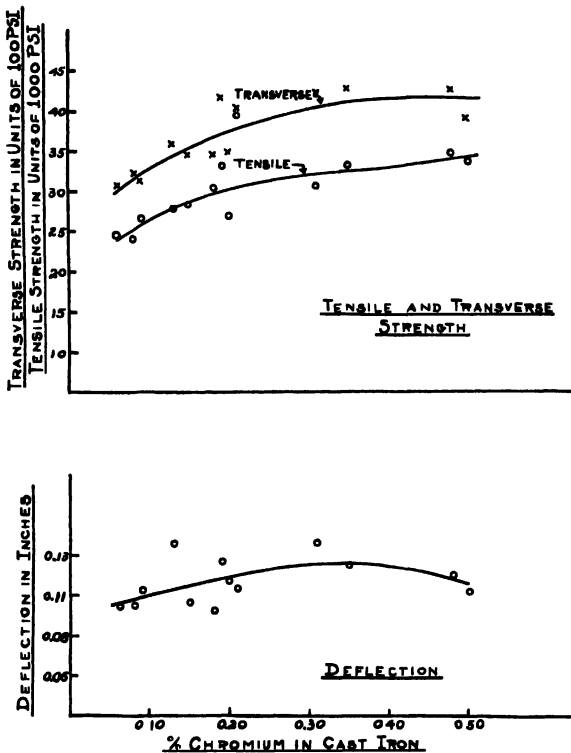


FIG. 4.—EFFECT OF CHROMIUM ON TENSILE AND TRANSVERSE STRENGTH AND ON DEFLECTION.

Results obtained by Shipley are included for comparison. The different grades of cast iron show varying levels of physical properties but in every instance the strength of the irons has been increased by the addition of chromium. This improvement in strength varies from 5 to 31 per cent in the present tests, and is further confirmed by tests on the cupola heats plotted in Fig. 4, and the laboratory heats listed in Table 2. The

deflection is in general higher than that of the unalloyed iron until the chromium exceeds 0.50 per cent.

### HEAT RESISTANCE

The series of cast irons of test 1 containing from 0.03 to 0.52 per cent chromium were annealed for 3 hr. at both 650° and 750° C., and furnace-cooled. After the 650° C. treatment, the specimens were examined in regard to structure and hardness. It was found that the presence of 0.52 per cent chromium prevented softening, the final Brinell hardness being 192. The same stabilizing influence was exhibited to a lesser degree by chromium contents of 0.26 and 0.37 per cent, a hardness of

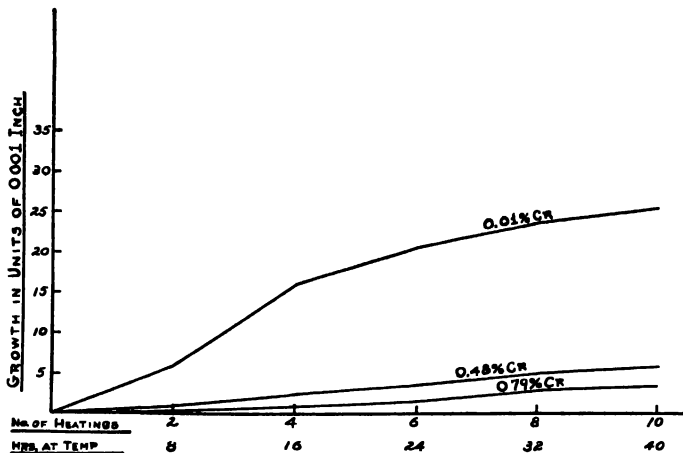


FIG. 5.—EFFECT OF CHROMIUM ON GROWTH OF CAST IRON ALTERNATELY HEATED AND COOLED FROM 600° C. (1112° F.).

168 and 180 respectively being maintained. The chromium-free iron submitted to this same treatment showed a drop in Brinell hardness to 140.

The influence of chromium on preventing excessive softening was even more evident after the 750° C. treatments. The hardness of the chromium-free iron fell to 110, while with 0.26 per cent chromium present a Brinell hardness of 140, and with 0.52 per cent chromium, a Brinell hardness of 180 was retained. This influence of small amounts of chromium on preventing excessive softening assumes particular significance when heat treatment, such as annealing to remove casting strains, is necessary.

In Fig. 5 is shown a series of curves illustrating the growth of the cast irons containing 0.01, 0.48 and 0.79 per cent chromium when alternately heated and cooled from 600° C. (1112° F.). The curves are based on the total increase in length of machined and ground cast-iron bars

1 in. in diameter and 6 in. long. It is evident from these curves that a small amount of chromium decreases the growth of cast iron to a remarkable degree.

The opinion that chromium considerably increases the wear resistance of cast iron is widespread, and this metal has been frequently added to cast irons that must resist abrasion. No wear tests were performed on the irons herein described owing to the difficulties involved in this type of testing. It is, however, pertinent to refer to the comprehensive investigation of the comparative abrasion loss of different cast irons made by Klingenstein, who shows the marked effect of chromium in lowering abrasion loss. This is evident with a chromium addition of 0.4 per cent. It has been demonstrated also that chromium cast irons are particularly suitable for castings subjected to sliding wear at elevated temperatures, because of their increased resistance to heat.

### MACHINABILITY

Closely connected with the hardness of cast irons treated with chromium is the question of machinability. In the present work no difference in machinability was noted with additions of chromium up to approximately 0.80 per cent. In addition, machining tests run by an independent machine shop on the various steps of the telescope castings previously described failed to show any definite variation in machinability between the chromium-free and chromium-bearing castings in the various thicknesses. This fact has been checked by other experience and is particularly stressed because of various current opinions to the contrary. These opinions are generally based on work with irons of appreciably lower silicon content than the optimum. No marked drop in machinability has been noticed in chromium cast iron until its hardness approaches 285 Brinell. However, this is true only of cast iron in general if the hardening is brought about by chromium additions, and not true if the iron is hardened by lowering the silicon content, by reducing the section size, or by chilling.

### INFLUENCE OF SMALL CHROMIUM ADDITIONS ON THE STRUCTURE OF CAST IRON

In the experiments carried out in this investigation, it was particularly noticed that a small addition of chromium was effective in rendering the cast irons completely pearlitic. These irons, in the absence of chromium, contained an appreciable amount of free ferrite. For example, 0.26 per cent chromium was sufficient to render cast iron 2-A of test 1 almost completely pearlitic as cast in the standard arbitration bar.

This pearlitizing action of chromium is sufficiently strong to preserve a pearlitic structure even when the section of a casting was considerably

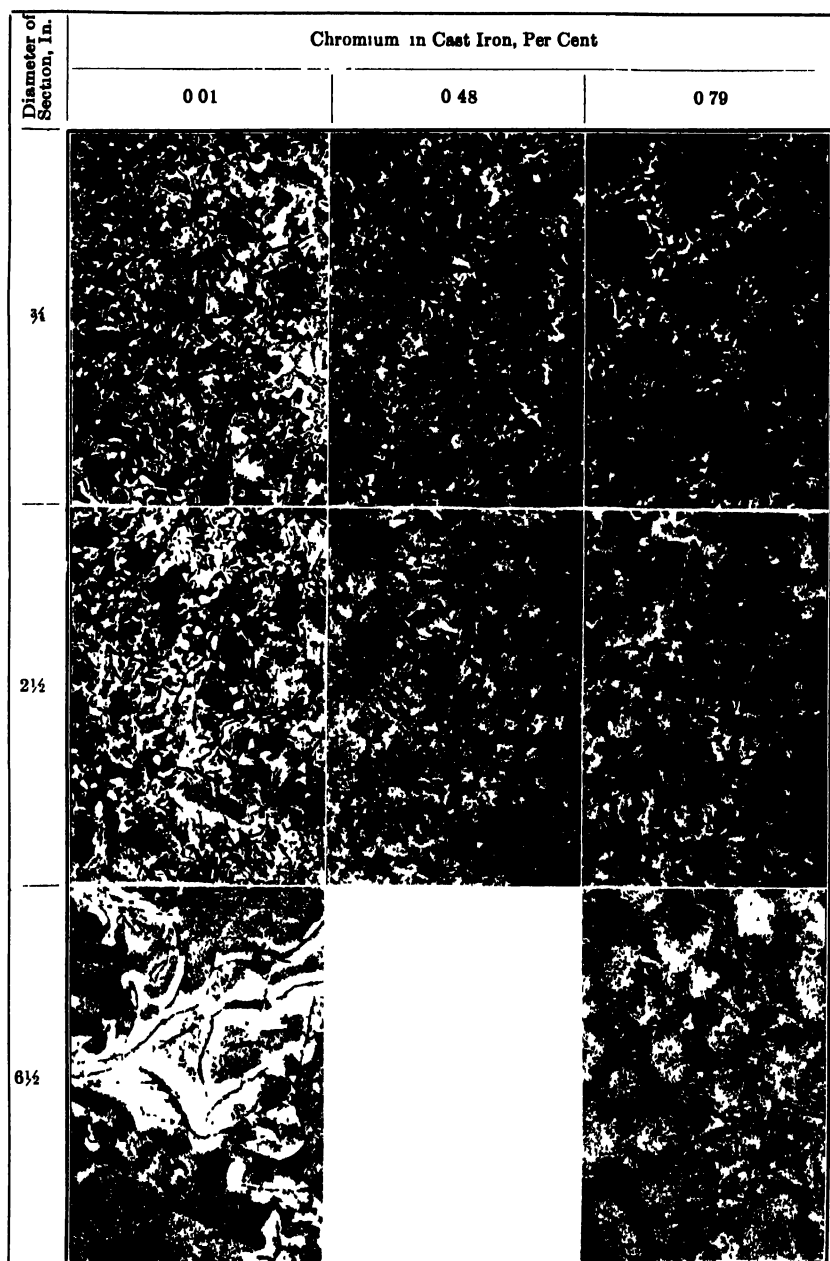


FIG. 6.—INFLUENCE OF SMALL CHROMIUM ADDITIONS ON THE STRUCTURE OF CAST IRON OF VARYING THICKNESS.  $\times 100$ .

Reduced one-third; original magnification given.

increased, as illustrated in Fig. 6. The photomicrographs show the structures of the irons listed in test 2, when cast in sections  $\frac{3}{4}$  in. and  $2\frac{1}{2}$  in. in diameter, and when cast in heavy sections  $6\frac{1}{2}$  in. in diameter, in heats A and C.

In addition, chromium stabilized and maintained a pearlitic structure even on exposure of the cast irons to relatively high temperatures, as was evident in the annealing tests previously described.

This specific effect of small amounts of chromium on the structure of cast iron undoubtedly explains to a large extent the results obtained in the present experiments, as a pearlitic cast iron is considered the most suitable for high strength, density, and wear resistance accompanied by good machinability.

It has been reported by other investigators that chromium refines the graphite. This observation has been found to be true in regard to cast irons tending to form large graphite flakes, but in the present tests it was particularly noticed that the presence of chromium produced in addition a more uniform distribution of graphite and tended to prevent the formation of objectionable ferrite areas containing eutectic graphite.

#### SUMMARY

The addition of small amounts of chromium (0.25 to 0.50 per cent) produces a definite improvement in the strength, deflection and density of the cast irons investigated. On the addition of chromium, there is marked improvement in uniformity of hardness in varying sections, particularly with respect to the retention of hardness in heavy sections.

A distinct improvement in the heat-resisting properties of cast iron is effected by the addition of a small amount of chromium. This improvement is related to a stabilization of the pearlitic structure of the irons and an increased resistance to growth at high temperatures.

The machinability of cast irons containing small amounts of chromium is not adversely affected even though the hardness is moderately increased.

#### ACKNOWLEDGMENTS

The author wishes to express his appreciation of the interest shown in this work by Mr. F. M. Becket, President, Mr. J. H. Critchett, Vice-President, and Mr. A. B. Kinzel, Chief Metallurgist, of the Union Carbide and Carbon Research Laboratories. The aid of Mr. S. M. Norwood in supervising the cupola heats and Mr. J. R. Vilella in preparing the photomicrographs is herewith acknowledged. The cooperation of the foundries at which the cupola heats were prepared is particularly appreciated.

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## DISCUSSION

(George B. Waterhouse presiding)

G. F. COMSTOCK, Niagara Falls, N. Y. (written discussion) — Mr. Burgess has presented an interesting paper, giving decidedly worth-while information regarding the possibilities of chromium in cast iron, and results recently obtained in our laboratory agree with his data quite well. We did not, however, find so much increase in strength as he reports, and in our electric-furnace iron chromium decreased the deflection. Our methods and results will probably be published in detail later, but perhaps the brief tabulation below, showing what was obtained with chromium, may be of interest in connection with this paper. Each strength value given is the average of from five to eight specimens

Kind of Iron	Melting Furnace	Composition, Per Cent				Mechanical Properties			
		Total C	Comb C	Si	Cr	Transverse Strength, Lb	Deflection, In	Tensile Strength, Lb. per Sq. In	Brinell Hardness
Plain. .	Cupola	3 49	0 50	1 78		4,115	0 132	30,860	187
Alloy	Cupola	3 49	0 64	1 68	0 32	4,340	0 138	33,780	192
Plain	Electric	3 46	0 55	2 09		4,450	0 153	33,820	187
Alloy	Electric	3 47	0 73	2 10	0 56	4,823	0 145	36,520	207
Plain .	Electric	3 17	0 68	2 24	Trace	4,400	0 125	38,840	196
Alloy.....	Electric	3 18	0 83	2 23	0 72	4,390	0 107	43,020	223

My results on comparative microstructures were similar to the author's, but he has not told the whole story regarding the effect of chromium on the microstructure of gray cast iron. The most noticeable and consistent effects of chromium found in

our laboratory were, first, a marked refinement of the lamellar pearlite structure, the pearlite in chromium-bearing iron being largely sorbitic; and second, the presence of hard white areas in the normally spotted steadite (the phosphide eutectic). Presumably these white spots are chromium carbide, but I always found them in the steadite, not isolated by themselves, in the chromium-treated samples. Of course a higher magnification than the author used is required to observe these two effects to the best advantage. They are probably more important than the slight effect of chromium on the graphite flakes, and the strengthening derived from chromium additions is best explained by the sorbitizing action on the pearlite.

Another very important point, regarding chromium in cast iron, which the author has not mentioned, is its tendency to promote whiteness of thin sections. Our experience has shown definitely that chromium has a marked tendency to retain carbon in the combined form, so that if a casting is poured under such conditions of composition or cooling rate as would almost make it partly white, the addition of chromium to the iron would surely result in the occurrence of hard white spots in it. This is a serious matter in castings that are machined, and the prevalent use of nickel, which is a graphitizer, with chromium in cast iron is chiefly for the purpose of overcoming that difficulty. This point should certainly be mentioned in any discussion of chromium in cast iron, even though it may be somewhat unfavorable to the use of that alloy alone.

R. JOB, Montreal, Que. (written discussion).—It is a fact well known to all of us that during very recent years remarkable developments have taken place in the metallurgy of cast iron. A part of this is due to systematic chemical control, and better knowledge regarding the influence of the various constituents upon the physical properties of the metal, but an important part results from investigation of various alloys, particularly nickel and chromium. Mr Burgess's paper gives useful information regarding chromium and summarizes physical characteristics that have been found.

Many of the facts cited invite detailed discussion, but I will merely mention the statement that "a small amount of chromium decreases the growth of cast iron to a remarkable degree." This brings to mind some experiments that were made upon the Canadian National Railways with grate bars. Bars of ordinary cast iron were made at the foundry, and others of similar composition but with various additions of chromium, the latter being added in the form of ferrochromium (70 per cent Cr) from a funnel upon the spout of the cupola. Also, a steel grate bar was taken, containing about one per cent each of chromium and of nickel. Also, through the courtesy of Mr. E. K. Smith of the Electro Metallurgical Co., a bar of cast iron containing about 16 per cent chromium was obtained. These bars were all placed for several weeks in an annealing furnace used for heat treatment of locomotive forgings. In this way variations of temperature up to about 1500° F. were obtained daily during operation. Careful measurements of the bars were taken at the start and after final removal from the furnace.

Under these conditions ordinary cast-iron bars increased in length about  $1\frac{1}{4}$  in. in a length of about 3 ft.; the cast alloy steel,  $\frac{1}{4}$  in.; 0.49 per cent chromium cast iron,  $\frac{1}{2}$  in.; while cast iron containing 1.2 per cent chromium showed no growth, and the cast-iron bar containing 16 per cent chromium showed no growth and appeared to be unaffected by the treatment. These results are striking and give an indication of the increased service life that may be obtained at small cost by very moderate ladle additions of chromium.

The use of chromium in cast iron in connection with heat treatment also opens up an interesting field for development and promises greatly increased life of parts subject to abrasion, with consequent lowering of cost of maintenance.

D McLAIN, Milwaukee, Wis. (written discussion).—Many who read this paper will feel thankful to Mr. Burgess if he will kindly explain the methods by which the low total carbons referred to in Table 1, test 2, were obtained, as under standard cupola practice it is understood to be practically impossible to obtain 2.80 unless 90 per cent or more steel is used. A practical and technical foundryman whose practice is operating under laboratory control claims that in 25 years he has checked but one report in which the total carbon was under 3 per cent. In my own work, using up to 50 per cent steel in straight cupola melting, in the past two years I can locate only two reports, in which one was 2.98 and the other 2.96 per cent.

Tensile strengths of 50,000 to 60,000 lb. are obtained by using 50 per cent or more steel in air, electric furnaces, by the Emmel process, in producing high-test iron in cupolas, with total carbons of 2.50 to 3 per cent with or without alloys.

W. M SAUNDERS, Providence, R. I. (written discussion).—There is a general acceptance of the fact that chromium, even in small amounts, increases the tensile strength, heat resistance, and as far as comparative tests show, the wear resistance. Some of the author's conclusions, however, are open to criticism, and while there has been little work published on the effect of small percentages of chromium in cast iron, many foundrymen have ideas at variance with the author's claims. These may, or may not, be notions, but they are firmly fixed in the attitude of foundrymen toward chromium. There is, for instance, a decided difference of opinion regarding the machinability of cast iron containing chromium, and much blame for poor machining qualities has been rightly or wrongly laid to the presence of chromium.

Specific criticism of the paper may be directed toward the statement that small amounts of chromium influence the distribution of the graphite flakes. Here, again, differences of opinion exist, and the results do not appear to offer conclusive evidence that chromium alone is the cause of the even distribution mentioned. So many other factors may be responsible, such as silicon, actual amount of steel that has melted to form the mixture to be cast, degree of superheat when melted, as well as pouring temperature and cooling rate. Presumably the last two factors were kept constant in the various tests made, but in my opinion the degree of superheat is of great importance in determining the size and distribution of graphite in cast iron made with high percentages of steel.

In Fig 3, the tensile strength, deflection, and transverse strength are plotted for the irons in test 1. The wide variation of silicon in these four irons should not be overlooked. Nos. 1-A and 4-A are comparable, but 2-A and 3-A should not be included, except in a general way. It seems safe to assume, however, that if the silicon in No. 3-A had been of the same magnitude as in 1-A, the physical properties might be even higher.

As a matter of value to those interested in the microstructure of cast iron, some photomicrographs at higher magnifications would have been helpful.

R M. BLOOD, Boston, Mass. (written discussion).—The transverse-strength figures as given on Tables 1 and 2 seem low when compared with tensile strengths, even with the latter as low as they are shown under test 1. Moreover, the tensile strength and hardness figures for this test are lower than the writer would expect for an iron having a total carbon around 2.80, even with a silicon over 2.25 per cent.

In discussing the effect of section size on hardness (p. 41), the statement is made that "the presence of only 0.48 per cent chromium is sufficient entirely to prevent softening on an increase of section from  $\frac{3}{4}$  to  $2\frac{1}{2}$  in," in a telescope casting. Does the author mean that the hardness of these two sections would be the same? The writer would not expect this to be the case.



J. T. MacKENZIE, Birmingham, Ala.—I think Mr. Burgess's conclusions in the main are correct, but I do not think he has sufficiently emphasized the fact that this was practically all high-silicon iron. Cast iron is strongly affected by chromium when we have a critical composition such as a low-silicon iron. For instance 0.5 per cent chromium in a pipe with 1 per cent silicon will throw the whole thing white. We use it for rolls of different kinds with the Brinell hardness around 300 to 350. It takes only 0.5 per cent chromium to throw the combined carbon from 0.75 to 3.25.

I cannot understand the results shown in Table 1; with the analysis shown, I should have expected the tensile strength to be at least 50,000 lb. on the plain iron instead of 25,000. The arbitration bar with that metal, as normally made up, would go well over 5000 lb. While the strengthening effect to the chrome is probably in the right proportion, it is inconceivable to me that the cast iron of that composition could have shown that Brinell and those tensile strengths. Test 2, of a similar analysis, is getting up at about the right range—36,000 tensile with 41,000 tensile on the chrome-bearing iron and the Brinell hardness is approximately correct.

The same thing is true in Table 2. With the total carbon at 2.5, there is a tensile strength of 29,000 lb. One possible explanation is in the casting temperature, which is given as 1250° C., and with 2.5 per cent carbon, that is well below the liquidus line. If those temperatures are correct, I would not expect good castings from that analysis.

I do not like the word "porosity" when a shrinkage is referred to. There has been considerable discussion on that point.

I would like to take this opportunity of acknowledging Mr. Vilella's work on the photomicrographic examination of cast iron. I think he has shown that most of our published photomicrographs of cast iron show greatly enlarged holes where the graphite has been. In consequence of his work on polishing we may expect to change our ideas on photomicrographs in the future.

J. S. VANICK, New York, N. Y.—I join Mr. MacKenzie in expressing doubt about Table 1. I think the whole thing would be cleared up if in Table 1 the total carbon column were marked "Graphitic Carbon," the combined carbon in the following, then adding up to the total carbon in a third column. That probably would clear up the matter of strength properties.

Shipley's irons, as I remember them, will run in the range of 38,000 lb. tensile. They are either automotive or cylinder casting types. I do not know which one was chosen for this table, but an automotive iron usually will run from 3.10 to 3.40 carbon total.

E. K. SMITH, Chicago, Ill.—People ask, "What percentage of chromium will give the maximum strength or the best machinability, or the greatest wear resistance?" I think that one point one would want to consider, that comes up in practice, is—you have to take into consideration the factors that tend toward graphitization or toward carbide-forming characteristics. The maximum amount of chromium should be regulated according to the silicon, the cooling rate, the amount of carbon, the sulfur-manganese ratio, and so forth.

F. L. WEAVER, Buffalo, N. Y.—Recently a practical test was made on the effect of small percentages of chromium in cast iron, in that 0.35 Cr was added to a specific casting on a more or less semiproduction basis. The primary purpose was to retard growth on repeated heating and cooling, which was remarkably pronounced in comparison with regular cast iron, by heating repeatedly to 1600° F. the entire large casting, and measuring growth in all dimensions.

It is not uncommon to have white iron in very thin fins along parting lines and against inset cores, which adjoin sand surfaces to be machined, without machining difficulty, whereas, in the chromium castings—a too frequent occurrence of difficult

machining and tool damage prompted a suspension of its use. In the cases of tool damage, it was found that the white iron had extended from the thin fins back into the sharp corners of the casting itself.

The normal variation of the common impurities (beneficial or detrimental) such as manganese and sulfur, in cupola iron during continuous pouring, may have their influence with chromium in promoting this extension of chill from thin to sharp-cornered thick section. However, the addition of 0.35 copper, added for another purpose (corrosion), reduced this tendency toward chill, without apparent effect on strength, deflection, or the influence of chromium in retarding growth.

Aside from the above, the effects as given by Mr. Burgess have been borne out well on a practical basis.

J. T. MACKENZIE.—May I add one word on the general subject of cast iron? It is so complex and there are so many different analyses and grades of cast iron, that I think the authors of the paper would get out of a lot of difficulty by using the past tense and saying that 0.50 chromium *did* raise the strength of this cast iron so much, and not that it *does*.

C. O. BURGESS (written discussion).—It is interesting to learn that Mr. Comstock has confirmed the strengthening effect of small additions of chromium. From his table it is evident that his chromium-treated irons show a general increase in strength ranging from 6 to 11 per cent, although some of the irons contain as low as 1.68 per cent silicon. In only one case, where 0.72 per cent chromium was added to an electric-furnace iron, is there no evidence of increase in transverse strength, although the tensile strength of the same iron is increased 11 per cent. In regard to the structure of our irons, although chromium produced some structural refinement, the treated irons were not entirely sorbitized, the most notable effect being a more even distribution of graphite and the elimination of fine graphite-ferrite patches that are not resistant to wear and are starting points for corrosive action on the irons. In regard to chilling effect, as chromium is a carbide-forming element, a specimen verging on a white iron may be rendered white by the addition of an excessive amount of chromium. In this regard it has been conclusively demonstrated that 0.40 per cent chromium may be safely added to 1-in. bars containing as little as 1.5 per cent silicon without adversely affecting machinability, and with higher silicon content (2.05 to 2.11 per cent), as shown by Shipley, an equal amount of chromium can be advantageously added to sections down to  $\frac{1}{4}$  in. in thickness.

In regard to Mr. Saunders' remarks, it is true that in a number of cases rightly or wrongly chromium has been blamed for poor machinability. Usually this is undoubtedly due to the use of this element with other alloying elements that also serve to harden the matrix, and because its use has been abused, i. e., too large amounts have been added to cast irons verging on a white structure. In regard to the influence of chromium on graphite, none of the irons was superheated but the graphite was definitely better distributed because of the presence of chromium. I agree with Mr. Saunders that the physical properties would be even higher in the chromium-treated heats 2-A and 3-A with lower silicon content, but despite this fact the results serve to illustrate the strengthening effect of chromium. As Mr. Blood and Mr. MacKenzie point out, the physical values on all irons in test 1 appear relatively low. This is probably due to factors such as the type of melting and the condition and analysis of the scrap cast iron, only remelted scrap being used in these heats. However, the effect of chromium on the heats is directly comparable, as the same scrap and method of melting was used in every instance.

In answer to Mr. Blood's question, the hardness of the  $\frac{3}{4}$ -in. and  $2\frac{1}{2}$ -in. sections of the cast iron in test 2 containing 0.48 per cent chromium was the same. The

explanation for this can be seen in the photomicrographs of Fig. 6, this cast iron remaining completely pearlitic and retaining its fine structure even in the heavier section.

It is gratifying to find that Mr. Job has confirmed the effect of small amounts of chromium on decreasing or eliminating growth in grate bars even at 1500° F. It would seem that any cast iron intended for thermal resistance or strength should necessarily contain chromium. I agree with Mr. Job that heat-treated chromium cast irons would produce increased life at low cost in parts subjected to abrasion.

In regard to Mr. Smith's remarks; in general the silicon content and to a minor degree the total carbon content have an influence on the optimum chromium content, but this is not critical. For example, 0.50 per cent chromium may be normally added to any cast iron containing 1.75 to 3.00 per cent silicon, 2.75 to 3.75 per cent carbon, with beneficial results.

Mr. Vanick is mistaken in regard to Table 1. The correct analyses of the irons are shown in this table. The analyses of Mr. Shipley's irons are summarized in the section on materials tested. Their physical properties are plotted in Figs. 1 and 3 merely to illustrate that the same physical relations as effected by chromium content have been found by another investigator using a somewhat different cast iron.

Mr. Weaver's use of 0.35 per cent copper with chromium to combat corrosion is of interest, although it is difficult to see how this small amount of copper can have a marked effect on reducing chill.

Mention has been made regarding the relatively low total carbons in the cupola irons in test 2, Table 1. These heats were made by a foundry according to its regular practice, and similar carbon contents are reported as being readily obtained. Many foundries have produced irons in this carbon range, the ordinary method being the use of high blast pressure coupled with the minimum amount of coke and relatively high percentages of steel in the mixture. It was considered fortunate that irons of these carbon contents could be investigated together with the irons containing 3.60 to 3.92 per cent carbon, as it gave us a wide carbon range in which to study the effect of chromium.

# An Improved Nickel-chromium Hardened Chilled Cast Iron

BY J. S. VANICK,\* NEW YORK, N. Y.

(New York Meeting, February, 1933)

AN extremely hard, tough, and strong, white or chilled cast iron has been applied for the past several years to industrial and mining services in which its unusual properties have been confirmed by its ability to deliver in many instances much better performance than plain chilled iron, or other wear-resistant materials. It is being produced regularly by alloying a good base composition of chilled or white cast iron with essentially 4 to 6 per cent of nickel and 1 to 2.5 per cent of chromium. Such a material can attain a hardness exceeding 600 to 750 Brinell as against 380 to 530 for corresponding grades of plain chilled iron. The strength is approximately doubled and the toughness significantly increased. These properties make it especially useful for many applications requiring a high hardness for resistance to wear, abrasion, attrition, deformation; to some extent to high compressive loading and to a lesser but important degree to corrosive action. A wide variety of commercial castings is being successfully produced from this iron, ranging in size from the small grain-grinding plates or burrs through medium-sized castings such as sand pumps up to large, heavy castings such as rolls for metal rolling or cement grinding.

The composition of this white cast iron may be roughly bracketed within the range shown in Table 1.

TABLE 1.—*Composition of Improved Nickel-chromium White Cast Iron*

	General	For Maximum Strength (Low C)	For Maximum Hardness (High C)
Total carbon, per cent	2.60–3.80	2.60–3.20	3.20–3.80
Silicon, per cent . . .	0.15–1.50	0.40–1.50	0.15–1.20
Nickel, per cent	3.0–6.0	3.0–5.0	3.5–5.0
Chromium, per cent	0.50–2.50	0.50–1.50	1.2–2.5
Manganese, per cent	0.15–1.50	0.15–0.60*	0.15–0.60*

\* Optional; up to 1.50 Mn under certain conditions.

\* Development and Research Department, The International Nickel Co., Inc.

## MELTING AND CASTING OF EXPERIMENTAL HEATS

The need for producing iron under identical conditions for comparable results was clearly established in earlier work, and the same procedure was applied in the melting and casting of these experimental heats. A furnace with capacity enough to hold all of the plain iron necessary was used to melt down the charges of pig and scrap. This bath then acted as a reservoir from which successive taps were taken, alloyed, brought up to pouring temperature, and cast. Chill blocks, measuring 2 by 4 by 6 in., 2 by 6 by 6 in., and in some cases 6 by 6 by 9 in., were cast. These blocks were chilled on their 2 by 4, 2 by 6, and 6 by 6-in. faces, respectively, and subsequently were split open so that the details of the fracture could be noted.

Square-sectioned bars chilled on one side or opposite sides were cast for transverse strength tests. Cylinders,  $2\frac{1}{2}$  in. in diameter, from the core of which test bars were taken, were used to determine tensile properties, as well as specimens cored from the grayed portions of the large 6 by 6 by 9-in. chill blocks. Hardness tests, usually Brinell, were taken over the clear white or clear gray zones of castings poured from the same heat. Hundreds of cupola heats subsequently demonstrated the practicability of producing this type of iron, and added further detailed data as to its characteristics.

Carefully made tests run in the Amsler wear-testing machine at a load of 20 kg. corresponding to a wheel or line contact pressure of 20,000 lb. per sq. in. show plain chilled cast iron wearing away 5 to 12 times faster than the same metal fully alloyed (4.5 per cent Ni, 1.5 per cent Cr) for maximum hardness. Figs. 10 and 11 record some of the results.

## EXPERIMENTAL DATA, COMMERCIAL PRODUCTION AND APPLICATIONS

Steels containing about 5 per cent of nickel long ago established their worth in gears subjected to severe duty, and the hardening effect that is developed in case-hardened steels of this type was expected to occur in the body of chilled cast irons. However, the fact that nickel reduced the chill prevented the applicability of nickel alone. The striking ability of nickel to harden the clear chill of cast iron while the depth of chill was decreasing brought to light important possibilities in improving chilled irons by alloying. Tables 2A and 3A, and Fig. 1, illustrate the chill-reducing power of nickel in typical irons high and low in total carbon. The inverted positions of strength and hardness for high and low-carbon contents, and the gradual improvement in hardness and strength with increasing nickel content, indicate that, in either case, the body or matrix of the iron is being acted upon by the non-carbide-forming nickel. The comparatively high strength and hardness values attained with 3 to 6 per cent additions of nickel indicated clearly that maximum results

would be obtained in that range. It was still necessary to develop the proper depth of chill and control its texture to prevent spalling, cracking, or surface checking, to make this improvement valuable. The fact that chromium was a powerful chill producer and that approximately three parts of nickel balanced one of chromium in low-silicon irons had previously been established. Moderate additions of nickel and chromium made in this ratio produced approximately evenly chilled irons; that is, irons chilled to an equal depth of clear white. Experienced rollmakers proved that moderately stronger and harder castings would be produced by balanced nickel-chromium additions with properties corresponding to results shown in Tables 2B and 3B. This effect parallels that developed in alloyed gray irons and is known to be associated with a fundamental strengthening and hardening of the body or matrix of the iron.

TABLE 2.—*Chill, Strength and Hardness of High-carbon Alloyed Iron*

No.	Total Per Cent	Si, Per Cent	Ni, Per Cent	Cr, Per Cent	Chill Block			
					1½" Sq	2 × 6 × 4		
					Depth White	Depth	Hard- ness	Back
A. HIGH-CARBON, ALL-NICKEL SERIES								
562	3 62	0 65			Full	2 00	464	269
578	3 63	0 66	0 19		Full	1 80	474	217
570	3 69	0 70	0 30		1.00	1 70	484	212
566	3 62	0 64	0 61		0 85	1 35	491	190
568	3 62	0 72	1 00		0 60	0 45	512	179
576	3 54	0 74	2 04		0 20	Gray	530	192
584	3 60	0 68	3 52		0 15	Gray	573	212
592	3 54	0 72	5 05		none	Gray	Gray	232
B. HIGH-CARBON, MILDLY ALLOYED NICKEL-CHROME SERIES								
572	3 56	0 64	0 33	0 14		1 55	477	286
580	3 64	0 60	0 67	0 14		1 40	477	216
574	3.68	0.60	0 66	0 27		1 75	505	261
588	3 68	0 62	1 12	0 28		0 85	512	196
582	3 64	0 71	0 63	0 41		2.10	495	311
590	3.60	0 71	1.10	0 46		1 50	555	217
C. HIGH-CARBON, FULLY ALLOYED NICKEL-CHROME SERIES								
676	3 57	1 04				0.45	495	190
654	3 47	0 97	1 51	0.59		0.70	560	235
656	3.49	0 98	1.53	0 89		1.70	555	286
662	3.46	1 02	2 89	0 84		0 85	584	316
666	3 52	1 02	4 34	0.85		0.30	652	387
668	3.48	1.01	4.20	1 44		1.25	713	460
674	3.36	1.02	5 72	1 47		0 50	652	402

TABLE 3.—*Chill, Strength and Hardness of Low-carbon Alloyed Iron*

No.	Total C, Per Cent	Si, Per Cent	Ni, Per Cent	Cr, Per Cent	Chill Block 2 × 6 × 6		
					Depth White	Hardness	Back
A. LOW-CARBON, ALL-NICKEL SERIES							
618	3.12	0.72			6 00	430	375
634	3.08	0.64	0.71		2 40	438	223
626	3.06	0.67	1.09		1 20	430	226
648	3.07	0.60	2.07		0 90	474	238
640	2.94	0.70	3.47		0 40	484	255
632	2.91	0.70	5.21		0 25	555	277
B. LOW-CARBON, MILDLY ALLOYED NICKEL-CHROME SERIES							
620	3.08	0.75	0.31	0.10	6.0	418	375
628	3.03	0.72	0.49	0.15	6 0	423	375
636	3.10	0.71	0.79	0.15	2 3	444	277
630	3.03	0.75	0.75	0.27	6 0	444	387
644	3.02	0.74	1.18	0.25	2 0	450	269
638	3.10	0.72	0.77	0.41	6 0	444	387
646	3.16	0.73	1.0	0.42	6 0	477	436
C. LOW-CARBON, FULLY ALLOYED NICKEL-CHROME SERIES							
680	2.79	1.00			1 45	418	163
690	2.78	1.09	1.05	0.45	2.35	460	350
692	2.73	1.06	3.22	0.89	3 00	532	430
694	2.63	0.85	4.66	0.75	2 20	578	495
696	2.79	0.93	4.50	1.43	6 0	625	520
700	2.73	0.86	5.96	0.74	1 25	555	477
702	2.71	0.95	6.39	1.57	2 25	585	387
710	2.83	0.94	7.88	3.09	6 0	512	364

Carrying the nickel-chromium additions into still higher percentages revealed that at about 4 to 6 per cent nickel and 1.25 to 2.50 per cent of chromium, a chill hardness that reached the very high values of 650 to over 700 Brinell in the clear white zones was developed, accompanied by a considerable refinement in fracture. A stronger and tougher core than was obtainable in plain or mildly alloyed irons—which nevertheless could be machined, although not with the same ease as the corresponding plain chilled iron cores—accompanied the chill improvement. Test pieces cored from the gray zones of large castings showed a strength about double that of unalloyed iron of the high-carbon type. Test pieces cast to size possessed tensile strength in the range of 60 to 100,000 lb. per sq. in., for the solid white iron. Summarizing these results, it is evident that the

highly desirable combination of surface (chill) hardness and core and chill strength in chilled castings has been obtained in the range of 4 to 5.5 nickel and 0.90 to 2.0 per cent chromium, as shown in Tables 2C and 3C and Figs. 2 and 3. It is this combination that is so useful to the consuming industries.

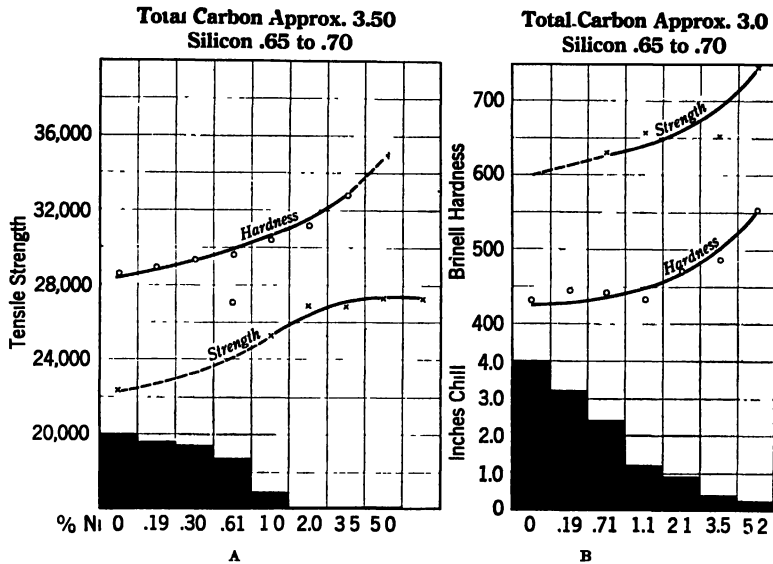


FIG. 1.—GENERAL EFFECT OF NICKEL ALONE UPON HARDNESS OF CHILLED FACE, TENSILE STRENGTH OF GRAY CORE, AND DEPTH OF CLEAR WHITE IRON CHILL.

### *Influence of Auxiliary Elements*

Manganese in excess of the amounts ordinarily present in white iron must be carefully introduced, because of its reaction with sulfur and possible after effects upon chill depth.

An addition of up to 1.5 per cent manganese with or without a compensating reduction in nickel produces a slightly weaker, but fairly hard, chilled face, as shown in Table 4A. An increase in manganese above this level is readily recognized in the fracture alone by a coarser, spiny fracture; and in the worst cases by a platy or spangled fracture accompanied by extreme brittleness. A softening of the chill, and a weakening in strength to abnormally low values below those for plain chilled iron, accompanies these effects.

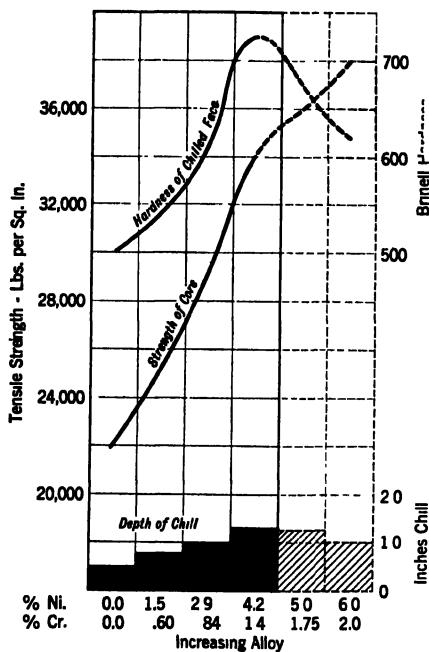
Molybdenum seems to exert a useful, stabilizing effect upon the hardness, structure and strength. Accompanied by chromium, the carbide-forming tendencies of molybdenum become more pronounced. A deepening of the chill and a softening of the chilled face occur as when there are excessive chromium, manganese, and similar elements.

Heats extremely low in carbon and high in silicon possess the power of being substantially hardened by additions of nickel and chromium, as



shown in Table 4C and 4D. It might be mentioned at this point that chill depth in these very low-carbon cast irons is considerably more difficult to trace. The hardening or martensitization of the cores or backs interferes with the broad application of these low-carbon compositions where machinability behind the chill is necessary.

**Total Carbon Approx. 3.5%**  
Silicon .95 to 1.0%



In Proportion Ni = 25 to 30 to Cr = 10

FIG. 2.

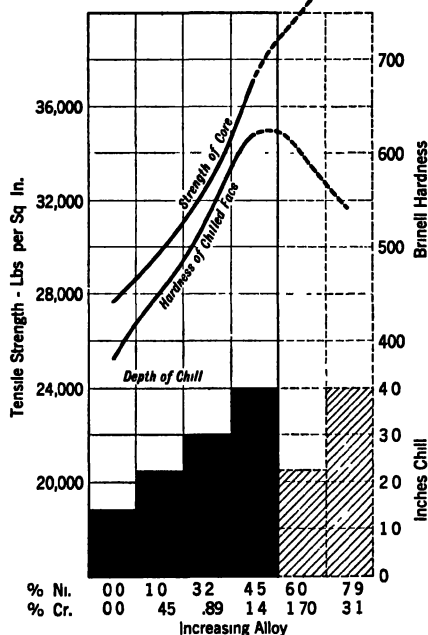
FIG. 2.—MAXIMUM HARDNESS OBTAINED IN RANGE OF 4 TO 5 PER CENT NICKEL AND 1.25 TO 2 PER CENT CHROMIUM.

Dotted lines represent properties of compositions alloyed in excess of needs for maximum hardness.

FIG. 3.—AS SHOWN IN FIG. 2, MAXIMUM HARDNESS IN LOW-CARBON TYPES OF CHILLED IRON OCCURS IN RANGE OF 4 TO 5 PER CENT NICKEL AND 1.25 TO 2 PER CENT CHROMIUM.

Dotted lines same significance as in Fig. 2.

**Total Carbon Approx. 2.80%**  
Silicon .90 to 1.05%



In Proportion Ni = 25 to 30 to Cr = 10

FIG. 3.

An excess of chromium, or a high-chromium composition not balanced by the correct amount of nickel, leads to effects similar to those produced with a high manganese; namely, brittleness, coarsening of the texture, and an actual softening of the chill accompanied by a mottling, or excessive carbide formation, in cores of heavy sections, destroying machinability.

A high nickel content leads to austenitization accompanied by softening and toughening and decreasing chill. Similar effects occur if an excess of nickel and chromium together is added, as shown in Fig. 2.

An interesting feature appears in the data of Table 5, which illustrates the fact that impurities such as sulfur, picked up through the usual process of cupola melting, may contribute to further improvement in hardness not available in the purer, air furnace melted, metal. Table 5B shows rather startling effects of high sulfur contents in deepening the chill and increasing the core or back hardness as in heats 2893 and 2895 while an increase in nickel content from 2.50 to 3.50 per cent raises the chilled face hardness sharply.

TABLE 4.—*Effect of Special Elements*

Type	Total C	Si, Per Cent	Ni, Per Cent	Cr, Per Cent	Mn, Per Cent	Mo, Per Cent	Chill Depth	Brinell Hardness, 2 × 6 × 6 Chill Block	
								Face	Back
A. EFFECT OF MANGANESE									
Ni-Mn-Cr	3 66	0 95	3 08	1 52	1 47		1 500	600	380
Ni-Mn-Cr	3 70	1 40	1 33	1 43	2 17		2 000	477	269
B. EFFECT OF MOLYBDENUM									
Ni-Mo	3 14	1 02	4 50		0 33	1 96	0 625	652	387
Ni-Mo-Cr	3 37	1 12	1 99	0 96		0 77	2 250	600	364
C. LOW-CARBON HIGH-SILICON TYPES									
Ni-Si . . .	2 40	1 42	1 30				1 500	430	
Ni-Si	2 32	1 71	1 98				1 500	444	
Ni-Si	2 35	1 36	2 60				1 500	460	
Ni-Si .	2 43	2 68	3 98				0 250	495	
Ni-Si . . .	2 48	2 42	4 36				0 125	600	
D. EFFECT OF NICKEL SILICON-CHROME									
Ni-Si-Cr. . .	2 57	1 37	2 91	0 66			2 000	482	465
Ni-Si-Cr.	2 50	0 85	4 66	0 75			2 200	578	

### *Comparison of Plain and Nickel-chromium Hardened Chilled Iron*

It is not possible in plain iron to secure a chill surface hardness much greater than about 500 Brinell, and it is necessary to use a high-carbon iron (3.50 per cent) to obtain such a value. Owing to the presence of much graphite, the gray iron core of a high-carbon chilled iron casting is weak and brittle.

Moderate additions of nickel and chromium, to the extent of 0.50 to 2.50 per cent nickel and 0.50 to 1.0 per cent of chromium, produce a marked improvement, but the maximum effect is obtained at approximately 4 to 6 per cent nickel and 1 to 2 per cent chromium. Castings of

TABLE 5.—*Effect of Sulfur*

No.	Total C	Si, Per Cent	Ni, Per Cent	Cr, Per Cent	Mn, Per Cent	S, Per Cent	Chill Depth	Block 1½ × 2 × 6 Chill	
								Face	Back
A. CUPOLA HEATS									
3189	3 55	1 03	2 97	0 87	0 35	0 071	0 375	588	320
3186	3 46	1 04	2 99	0 84	0 33	0 091	0 500	627	320
3184	3 52	1 03	2 94	0 90	0 34	0 105	0 625	652	340
3182	3 35	1.15	3 36	0 68	0 29	0 123	0 375	627	364
3179	3.41	0 57	2 80	0 87	0 32	0 143	6 00	650	530
B. LOW-CARBON (CUPOLA TYPES)									
2385	2 99	0 85	2 42	0 82			1 625	555	286
2893	3.03	0 66	3 60	0 46			1 320	627	340 <sup>a</sup>
2805	3 30	0 46	3 30	0 89			0 750	652	364
2895	3 15	0 74	3 62	0 92			all	683	495 <sup>a</sup>
C. FULL NI-HARD (MAXIMUM HARDNESS), CUPOLA HEATS									
2691	3 52	0 95	4 53	1 41			0 875	686	418
2845	3 11	0 85	4.69	1 38			1 625	652	418
2599	3 45	1 01	4 43	1 34			1 250	782	460

<sup>a</sup> Chill depth increase due to large portion car-wheel scrap in charge

this composition may be produced having a hardness of 550 to over 700 Brinell on the chilled surface and at the same time possess a core strength from 20 to 100 per cent greater than that of the plain carbon iron.

Table 6 summarizes the properties of low-carbon and high-carbon chilled iron with and without nickel-chromium additions.

TABLE 6.—*Typical Results*

	Plain Iron		Nickel-chromium Iron	
	High-carbon	Low-carbon	High-carbon	Low-carbon
Hardness of chilled surface, Brnell. ....	500	400	650-750	600
Tensile strength of gray core, lb. per sq. in. ....	16/25,000	22/30,000	30/35,000	35/50,000
Total carbon, per cent. ...	3.30/3 50	2.75/3 0	3 30/3 50	2 75/3 0
Silicon, per cent. ....	0 75/0 90	0 75/0 90	0 75/1.25	0 75/1 25
Nickel, per cent			4 50	4.50
Chromium, per cent. ....			1 50	1 50
Tensile strength of chill, lb. per sq. in. ....			60-80,000	80-100,000

It is evident that by the use of alloy it is possible to secure such a favorable combination of surface (chill) hardness and core strength in a chilled casting as is shown in the last two columns of Table 6. It is this combination that is considered commercially valuable.

The properties developed are highly desirable from the chilled-roll consumer's viewpoint and the same properties are greatly desired in grinding, crushing and conveying equipment.

*Structure.*—Chilled irons moderately alloyed with nickel and chromium reveal a gradual grain refinement corresponding with the amount of alloy used, but in the very hard composition, a distinct refinement in the texture of the chill is developed. The plain chilled iron is coarse and columnar, while the alloyed iron is fine grained and dull, indicating a much greater toughness and resistance to cracking or spalling as well as to shock or impact.

Plain chilled iron consists of a spongelike framework composed of iron carbide or cementite filled with a matrix of pearlite. The pearlitic matrix occupies more than one-half of the volume of the chilled zone and the effect of increasing amounts of nickel and chromium in moving this matrix into the sorbitic, troostitic and martensitic conditions is believed to be largely responsible for the increased hardness of the chilled surfaces.

The rather wide percentage range of nickel and chromium necessary to produce optimum properties is needed to provide for differences in cooling rates of castings of different sectional area or weight. The full 4.5 per cent nickel and 1.5 per cent chromium additions to high-carbon cupola-melted irons easily develop the extremely hard chilled surfaces.

*Fracture.*—The fracture of the chilled portion of an alloy chilled casting of the above composition is also characteristically different from that of a plain iron casting. Whereas the latter is coarse and columnar in appearance, that of the alloy iron is fine grained and dull, indicating a much greater resistance to shock and impact as well as resistance to spalling under load.

*Machinability.*—The low-carbon, high alloy described in the last column of Table 6 is practically unmachinable behind the chill, particularly if the section is less than 2 in. thick, the gray portion having a hardness of about 400 Brinell. If a low-carbon casting (under 3.0 per cent) with a machinable gray portion is required, the alloy content must be reduced to about 3.0 per cent nickel and 0.90 per cent chromium. Lowering the alloy content may entail some sacrifice of chill hardness, but the latter will still be well above that of plain high-carbon iron. Castings of high carbon content (3.30 per cent and over) are machinable without reduction in the alloy content in gray portions of reasonably heavy section; 4 in. or over.

*Corrosion Resistance.*—The fully hardened alloyed chilled iron possesses a marked resistance to corrosion compared to plain iron; thus add-

ing service life to castings which frequently suffer as much from corrosion as from wear, particularly in mine and chemical operations.

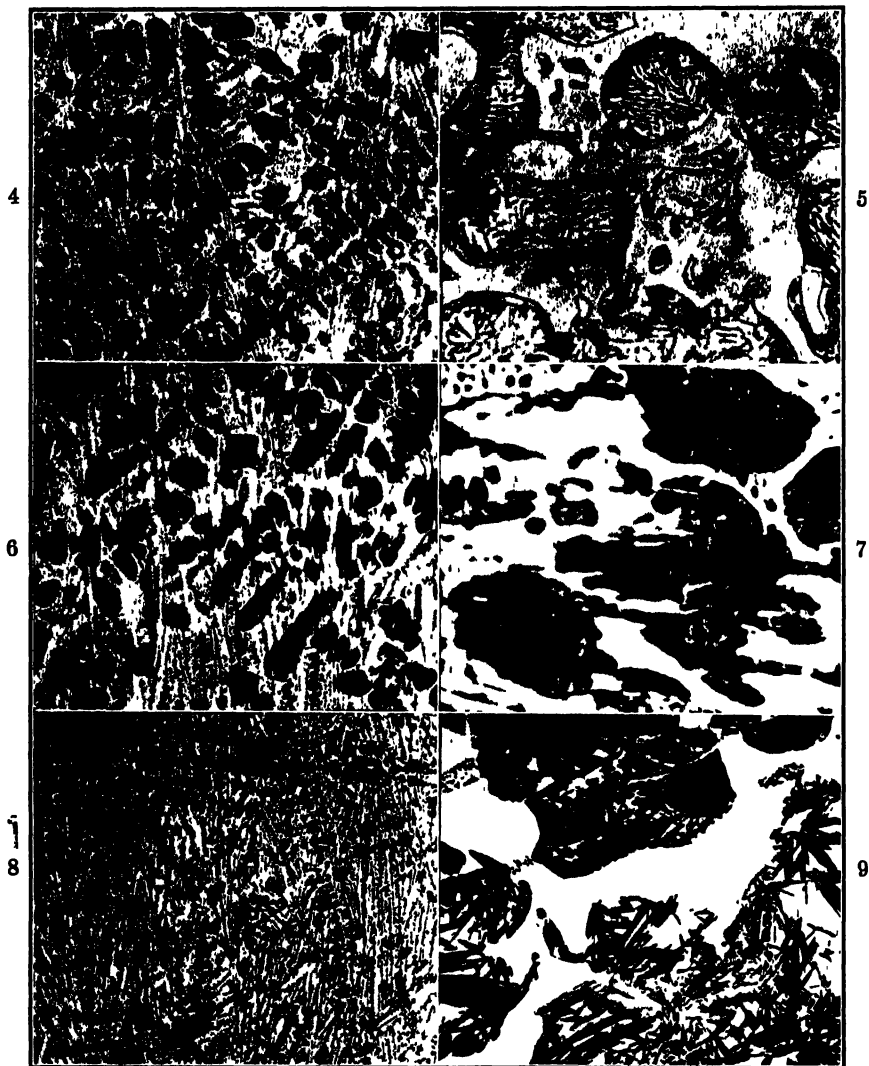


FIG. 4.—STRUCTURE OF PLAIN CHILLED IRON.  $\times 100$ .

FIG. 5.—PEARLITIC MATRIX OF PLAIN CHILLED IRON.  $\times 500$ .

FIG. 6.—STRUCTURE OF MODERATELY HARDENED (2.5 Ni, 0.80 Cr).  $\times 100$ .

FIG. 7.—TROOSTITIC MATRIX OF FIG. 7.  $\times 500$ .

FIG. 8.—STRUCTURE OF FULLY HARDENED (4.5 Ni, 1.5 Cr).  $\times 100$ .

FIG. 9.—MARTENSITIC MATRIX OF FIG. 9.  $\times 1000$ .

*Miscellaneous Useful Modifications (Semi-chilled Alloy Iron).*—Useful modifications of the 4.5 per cent nickel, 1.5 per cent chromium type of iron usually contain about one-half the alloy content referred to. They are

not as hard nor as resistant to wear as the fully hardened type, but they are important for such service as cement-mill liners, grate bars, and similar parts subjected to heat. In some instances the alloy content may be lowered to 1.5 per cent nickel and 0.60 to 0.90 per cent chromium and improvements over plain iron, with respect to wear and heat resistance, may be obtained.

Important details of the melting procedure, casting practice, physical properties, structure, relating to the fully hardened alloyed chilled irons, as well as their moderately alloyed companions, are described in the following paragraphs, along with successful methods of production, typical applications of the castings and their performance in service.

*Cupola Production.*—Moderately alloyed chilled irons can be produced in any foundry cupola by the simple procedure of adding the necessary nickel and chromium to the iron at the spout in the approved fashion. The amount of nickel and chromium added in this way rarely exceeds 5 per cent in all. The fully hardened alloyed irons containing 5 to 7 per cent of alloy require the presence of a large share of this alloy in the cupola charge, and this object is attained by using low-melting-point nickel in the form of F nickel, and bringing in the chromium by an addition at the spout; by using chromium briquets in the charge, or by means of specially alloyed chromium-bearing pig iron, like Mayari, for a portion of the charge. The application of the high-strength gray iron process,<sup>1</sup> modified to maintain the hard, chilled face, described in the last column of Table 6, has resulted in exceptionally strong cores or gray iron zones when strength has been a dominant factor. Sometimes a pig material containing nickel, chromium, and silicon in suitable proportions has been mixed with all steel scrap charges and melted in the cupola to produce a satisfactory product. This practice is particularly attractive to mining companies operating foundries that are located in remote regions where steel scrap and manganese steel scrap are relatively inexpensive or otherwise useless. Obviously these alloyed irons can be made readily in the air or electric furnaces, but cupola practice has been developed to produce them as well.

### *Applications*

One of the first applications of the hard, chilled nickel-chrome iron was for rolling-mill rolls. The performance of the fully hardened alloyed nickel-chrome chilled rolls on the harder, tougher metals has been vastly superior to ordinary iron rolls, and sometimes equal to hardened and ground steel rolls, naturally at considerably lower cost. The details of roll composition will be discussed in a future paper.

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<sup>1</sup>F. B. Coyle and D. M. Houston: High Strength Cast Iron. *Trans. Amer. Foundrymen's Assn.* (1929) **37**, 469.

Chilled wheels for street-railway, mine-car and crane-wheel service have been produced with roughly 50 to 200 per cent more strength in the gray sections and with a tough chill hardness capable of multiplying the resistance to wear, several times.

Experimental wheels of the fully hardened nickel-chrome type have been produced and put into service, while a considerable number of the mildly alloyed types of chilled wheels containing 2.5 to 3 per cent nickel and 0.60 to 0.90 per cent chromium have been produced and are being tested for their strength and wear resistance in conditions corresponding to those met in service.

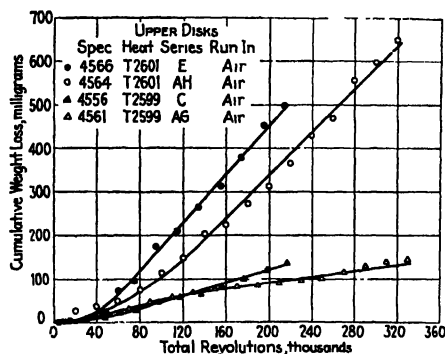


Fig. 10.—PLAIN CHILLED CAST IRON WEARS AWAY MORE THAN FIVE TIMES FASTER THAN NICKEL-CHROMIUM HARDENED CHILLED IRON WHEN IN CONTACT WITH ITSELF IN AMSLER WEAR TESTS. (D. E. Ackerman)

Heat T 2599: total C, 3.45; Si, 1.01; Ni, 4.43; Cr, 1.34.

Heat T 2601: total C, 3.52; Si, 0.85; Ni, none; Cr, none.

Castings for coal crushing, cement-clinker grinding, grinding-mill liners, grinding balls, and similar equipment requiring a high resistance to wear and abrasion, have been found to

outlast their plain chilled-iron predecessors as much as six to one. Sand and sludge pumps lined with the fully alloyed, chilled cast iron, replacing manganese steel, have given four to six months of service as against an equal number of weeks for the manganese steel. In a simple casting such as a sand-blast nozzle, a resistance to wear of five to six times that of plain chilled iron has been obtained. Tires for mullers and Chilean mills made of the alloyed iron and operating on crushed ore, clay or sand have outlasted several sets of castings of plain chilled iron in the same service. Rolling plates such as are used in the coal industry for conveying coal or screening coke as well as chutes used in conveying ore, sand, or other abrasive material, have economically displaced plain chilled iron in many instances, notwithstanding a higher initial cost of the castings. Often when gray iron has been

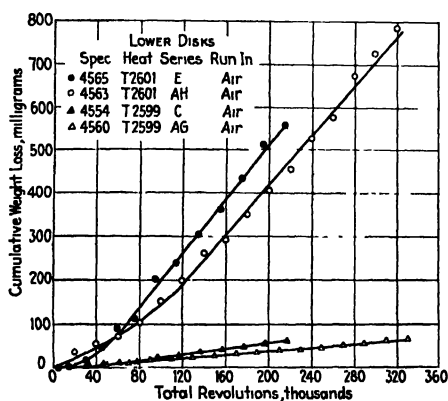


Fig. 11.—SAME AS FIG. 10. PLAIN CHILLED IRON WEARS AWAY 10 TO 14 TIMES FASTER WHEN SLIPPAGE, COMPARED TO FIG. 10, IS 10 PER CENT GREATER. (D. E. Ackermann)

required instead of chilled iron for such service, the fully alloyed, gray, hardened composition produced with gray-iron base higher in silicon has yielded an improvement comparable to that of the alloyed chilled iron over plain chilled iron. Centerless grinder-support blades, dies and pump liners are noteworthy examples.

#### ACKNOWLEDGMENTS

The author wishes to acknowledge particularly the work of Dr. P. D. Merica and Mr. T. H. Wickenden, who were associated with him in the development of this material. Acknowledgments are due especially to Messrs. E. J. Bothwell, D. E. Ackerman and T. J. Wood, of the laboratory staff at Bayonne, for their work upon the physical testing, wear testing, and cupola production of the irons described.

#### DISCUSSION

*(R. F. Harrington presiding)*

E. W. HARDING, Montreal, Que (written discussion) —The information in this paper is of an extremely interesting nature and forms a valuable contribution to our knowledge of the effects of variations in composition on the physical properties of the harder types of nickel-chromium cast iron. The effort made to produce iron under identical conditions is commendable in view of the desirability of making reliable comparisons between the various samples, and the obvious aim of the author to prepare samples in series with one variable factor will also be appreciated as enabling direct comparisons to be made. The figures given in Tables 2C and 3C indicate clearly the relation between the depth and hardness of chill and the carbon content. This information should provide a useful guide where these two factors are of importance, as, for example, in the production of chilled rolls. The extent of the influence of the carbon content on the depth of chill is particularly evident and it is apparent that for consistent results total carbon must be controlled within narrow limits.

In this connection the effect of carbon on hardness appears to call for comment. While it is undoubtedly true that increase in carbon produces a higher hardness on the chilled face it would appear to have the reverse effect on the unchilled back. For example, in alloys 668 and 696 (Tables 2C and 3C) in which the compositions are practically identical except for carbon content the hardness of the unchilled back was increased from 460 to 520 Brinell by a reduction in total carbon. This is supported in a comparison of alloys 666 and 694. The question naturally arises whether this effect would apply to a sand casting where no chill was applied. In our own experience with sand castings made in these alloys we have not found that high total carbon produces any definite increase in hardness, unless accompanied by a considerable reduction in silicon content.

We were particularly interested in the figures given showing the alloy contents at which maximum hardness was obtained. These figures confirm our practical experience and indicate that no advantage is gained by overalloying. In the production of small grain-grinding plates we have succeeded in obtaining Brinell hardness values of from 600 to 650 in unchilled sand castings without undue brittleness. Increase of nickel content in excess of 5.0 per cent does not produce any further increase in hardness, while beyond 5.5 per cent softening actually takes place. We have found, however, that a further increase in hardness results on raising the chro-



mium content to 2.0 or 2.25 per cent, but at or beyond this point brittleness becomes excessive.

We should have liked to have the author's comment on the relation between wear resistance and hardness in these alloys. There appears to be little practical information available on this subject and work on these lines would undoubtedly be of interest. The question whether wear resistance increases indefinitely with hardness or a limit exists beyond which increase in hardness is not accompanied by improved wear resistance is one that naturally arises in connection with grinding problems and on which more definite information is desirable.

The author's remarks on the effect of high manganese contents are interesting. In view of the mild carbide-forming action of manganese one might have expected a beneficial effect and we should like to learn to what extent this element could be used to replace chromium

Finally, we desire to congratulate the author on a paper containing practical information of value to engineers and foundrymen alike.

G. S. WILMOT, Weatherly, Pa. (written discussion).—We have had several years' experience in producing chilled iron alloyed with nickel and chromium, which has demonstrated that the material possesses much better properties than plain cast iron. Through the cooperation and assistance of the Bradley Pulverizer Co., of Allentown, Pa., we were able to develop a composition of the type described in the paper

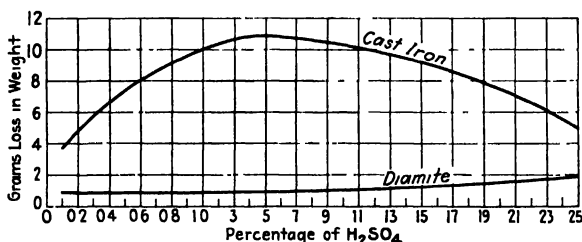


FIG. 12.—CORROSION RESISTANCE OF NICKEL-CHROMIUM CAST IRON AS AGAINST PLAIN CAST IRON.

and upon which careful service records were obtained for parts such as roll heads in pulverizing machines. For example, our composition of alloyed cast iron which we have trade-named "Diamite" is guaranteed to deliver more than 3000 hr. service and averages nearly 3600 hr.; whereas chilled cast iron will average about 1000 hr. In some cases, as much as 9000 working hours have been delivered with the Diamite roll heads. In the cement mills, we apply the material widely for roll heads, pushers, feed spouts, and hoppers, as well as chute liners, wear plates, or pocket mill liners in slug compartments in mills of the tube or ball type.

Good results have also been obtained in centrifugal pump castings used in the coal fields for handling sand, coal dust, or sludge, or similar abrasive materials and conveyor trough liners or pipe carrying suspensions of rock, coal or erosive fluids. In pumps handling ash around power plants, we have obtained records of pumps handling 375 tons of ash per day for more than 100 days as compared to an 18 to 30-day life for a special alloy steel previously used. In some cases such as this, corrosion is involved and we have tested the corrosion resistance of our nickel-chromium alloyed mixture, against plain cast iron, with the results shown in Fig. 12.

We feel that the resistance to wear or abrasion is of course most important, but in many cases equipment is allowed to remain idle and the better resistance to corrosion compensates adequately for the application of this material to such service. We feel that a distinct advance in the quality of chilled cast iron has been attained

in the development of material such as is described by Mr. Vanick. As the mining industry becomes more familiar with the performance of this material, we expect to see a considerable expansion in its use.

H. P. LANDROCK, Allentown, Pa. (written discussion).—I have read this paper with much interest. I believe that the field has been covered as thoroughly as possible at this time. About a year and a half ago, the Aldrich Pump Co. started to experiment with Ni-hard iron, mainly in an effort to duplicate our chilled plain iron plungers with less chance of loss and at a lower cost, by using nickel and chromium and omitting the chills. Our first heat of Ni-hard cast iron was cast Nov. 7, 1931, and it consisted of three pump plungers. Our first attempt was very encouraging in so far as hardness was concerned, but it was a complete failure when we considered the appearance of the castings. Owing to the quick cooling of the metal and the great shrinkage, which was all internal, we lost the three castings. We then duplicated the heat, changing our gating molding and pouring practice, and the second attempt was astonishing. By numerous experiments, both in cupola as well as molding practice, we not only have the Ni-hard cast iron production fairly well established, but we secure far better material, and a greater percentage of good castings than we did when using the old

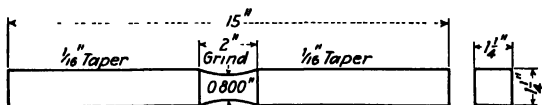


FIG 13.—TEST BAR FOR HEAT ANALYSIS.

conventional chilled iron cast in metal chills. We find the Ni-hard mixture much easier to control. It can be cast in green sand, and we are more sure of final results. We get an almost complete recovery from returns.

We remove gates and risers from castings with an acetylene nozzle, especially constructed for us by E. A. Smith, of the Linde Air Products Co.

Although we were unsuccessful at first in welding Ni-hard, we have developed a welding procedure whereby we can now weld it as well as regular cast iron.

The use of soft machinable inserts, which we have developed, has turned out very satisfactorily and we now machine, drill and tap castings the same as regular cast iron, except for somewhat lower speeds and feeds. The finishing of these castings is done by grinding wherever possible. When no grinding can be done, regular machining with Carboloy is resorted to, with speeds ranging from 8 to 60 ft. per min. Feeds varying from 0.006 to 0.032 in. per revolution and a depth of cut from  $\frac{1}{16}$  to  $\frac{1}{4}$  in. Some of the low-carbon, mildly alloyed irons are cut with regular high-speed tools.

So far we have had every important heat carefully analyzed in order to check the estimated against the actual analysis, and also to obtain data on deflection, transverse and tensile strength. We encountered difficulty in constructing test bars that could be clamped in the testing machine and stay in place. Because of the roundness of the usual  $1\frac{1}{4}$ -in. diameter by 15-in. bar the machine could not get a solid grip and would slip from the vise when pull was applied. We finally constructed a  $1\frac{1}{4}$ -in. square test bar, with slight taper toward the ends, then ground 2 in. in the center somewhat concave to a 0.800-in. diameter. That produced the necessary results. (Fig. 13.)

Table 7 gives the results upon 10 typical heats. Heat 6 was composed entirely of Ni-hard gates, risers and other Ni-hard returns. We frequently find test bars pulling at from 52,000 to 68,000 lb., with quite favorable results at times as shown in Heat 7.

We now make from Ni-hard cast iron a wide variety of castings, including pump plungers, pump casings, impellers, impeller wearing rings, liners, throat pieces, gears, rolls and disks for grinders, plowpoints, dies, molding and core plates, etc. The largest casting of Ni-hard produced here so far was a 6-ft pump shell which weighed 3960 lb.

finish-machined. Reports from customers indicate that they are well pleased with the wearing qualities of these Ni-hard castings.

J. T. MacKENZIE, Birmingham, Ala.—It seems to me that vanadium would be a very powerful element to investigate in this composition and it might possibly be that you could reduce the total amount of alloys by substituting vanadium for chromium and might even reduce the amount of nickel. Vanadium gives a very tough, hard chill and if you get the appropriate silicon and carbon content, it acts very powerfully indeed.

TABLE 7.—*Analyses of Heats*

Heat No.	Si, Per Cent	Mn, Per Cent	Ni, Per Cent	Cr, Per Cent	Total C, Per Cent	Shore Sclerometer	Corresponding Brinell Hardness Number	Deflection, In	Transverse Strength, In	Tensile Strength, Lb per Sq In
1	0.72	0.68	4.22	1.43	3.70	69	478			
2	0.73	0.75	6.07	2.56	3.10	74	514	0.06		55,000
3	0.94	0.45	4.27	0.81	3.40	61	401	0.08		63,000
4	0.90	0.80	6.12	3.12	3.58	92	682			
5	2.00		3.00	0.90		44	285	0.12	4,935	58,000
6	0.82	0.67	2.77	0.92	3.65	41	262	0.11	4,340	47,000
7	0.75	0.75	4.65	1.48	3.68	67	461			65,000 to 88,000
8	1.00	0.60	5.72	1.83	3.28	72 to 86	504 to 620			
9	1.16	0.69	4.38	1.45		66	452			
10	1.30	0.75	2.90	0.20	3.40	35	229	0.11	4,510	51,000

	Steel, Per Cent	Machined with	Speed per Revolution, Ft	Feed, r p m	Depth of Cut, In	Type of Casting
1	30	Carbology	25	0.010	$\frac{1}{16}$	Plungers
2	40	Ground				Plungers
3	30	Carbology	40	0.016	$\frac{3}{16}$	Grinding roller
4	50	Ground				Grinding disks
5	50	Ground	40	0.006	$\frac{1}{8}$	Gears (gray iron)
6	x	Ground	40	0.010	$\frac{1}{8}$	Diesel head (gray iron)
7	45	Ground				Pump liners
8	40	Carbology and ground	8	0.016	$\frac{1}{4}$	6-ft pump casing
9	40	Carbology	35	0.016	$\frac{1}{4}$	Pump parts
10	40	Carbology	50	0.030	$\frac{1}{4}$	Wearing ring

I should like to ask Mr. Vanick about the foundry characteristics of the iron, principally the fluidity and shrinkage. Can you handle that much chromium in a cupola, and if so, how much leeway do you have to give in the addition of those large amounts of chromium? I am principally interested, however, in the shrinkage and fluidity characteristics.

J. S. VANICK.—There is the possibility that vanadium might serve a useful purpose. We have not done very much with it, principally for the reason that it falls in the class of the carbide-forming elements. Their effect on the chill or depth of chill is all

pretty much alike after you have obtained the chill depth you want, which you can or might develop with appropriate amounts of vanadium, substituting it principally for some other carbide-forming element. Some improvement might be developed that way.

That, of course, is not true of nickel, which dissolves in iron in all proportions and exerts its effect in that unique way.

As for the production in a cupola, the usual procedure has been to use low-melting-point nickel pig in the charges, adding the necessary chromium in crushed form at the spout. This allows you to make sure that the chromium is coming in without any considerable loss. Some foundrymen like to use Mayari pig, which carries a certain amount of chromium and other alloys in with it.

I think some developments have been under way with the chromium briquette, but, to my knowledge, it has not yet attained sufficient popularity.

J. T. MacKENZIE.—How about fluidity?

J. S. VANICK.—The fluidity acts very much as it does in other irons of this kind of corresponding carbon contents. There has not been any difficulty in the running of very intricate castings; castings of the coffee-mill or feed-grinder burr type, which are really replacing cut and hardened steel. Those castings are run out to very fine points. Actual fluidity tests with this material have not been made.

So far as shrinkage goes, it has all the bad effects that chilled or white cast iron has. It shrinks very strongly—conforming to the high shrinkage of white cast iron, and it is susceptible to other risks in the foundry if the producer is not familiar with the antics of chilled cast iron or white cast iron.

J. T. MacKENZIE.—Can you cast this in green sand and get a white iron?

J. S. VANICK.—Yes, it is being cast in green sand as solid white iron. In many cases it has been produced that way to avoid the use of the chill which would be necessary in the ordinary product and which introduces additional risks that are not encountered in the green-sand casting.

J. H. HALL, High Bridge, N. J.—We have had a little experience in our plant with this material. Our iron-foundry superintendent died about the time we got going on it and we had to handle it almost entirely with steel molders. We are producing fairly difficult castings of this white iron in green sand with steel molders and men, and have had very little trouble in the foundry. Of course, it has a high shrinkage, but then steel has also.

We have had very little trouble with fluidity. In the melting of ferrochromium in the cupola, we did have at first a good deal of difficulty. We were afraid to add large amounts entirely at the spout, and made various attempts to introduce ferrochromium in the cupola. We got the amount of chromium we wanted, but we had rather an appalling loss, so, as Mr. Vanick says, we finally drifted over to the use of a large proportion of Mayari pig, adding the balance of the chromium at the spout. With the nickel, of course, there is practically no difficulty. You can put it in anywhere you please. The only objection to nickel is the cost. While speaking here before mining engineers, I want to comment on Mr. Vanick's remark that the merits of this material are set forward in the title, and must add that the demerits are in the foreword, in the first sentence. Many of those who are using this material are doing so in places where a very short time ago they used steels. If you tell a mining engineer or coal man or dredge operator you have something "tough," he thinks in terms of steel and very likely in terms of good, old Hadfield's manganese steel. Mr. Vanick calls this a "tough" white iron, but it is really pretty brittle. We have not had a great deal of difficulty with the breakage of these castings in the foundry and since

our men in the cleaning room got used to them and stopped hitting them with a hammer, we have not had much trouble there, but we did have trouble with them in transit and with the men who used them. It is sufficient to say that we crate these pieces and mark them "Don't drop."

As to the applications of this material, there is today a very interesting development in progress in the use of material to resist pure abrasion. The engineer dealing with abrasion associated with pressure, as in crusher jaws, has found manganese steel the solution of his problem, but in cases involving pure abrasion, manganese steel has never been entirely satisfactory. In some cases chilled iron, and in some cases hardened steel can be used, but there have been numerous instances where no material commercially available has been quite satisfactory, and of late there has begun a serious effort to develop a material that is as good for pure abrasion as manganese steel is for combined abrasion and pressure.

A case in point is the centrifugal pumps handling pure sand in the Chance classifiers which have been introduced in the hard coal region. They are a very acute problem. One solution of that problem is the use of these very hard nickel-chromium cast irons, which in castings of this size are white all the way through, and correspondingly hard and brittle. These castings, on the whole, have done fairly well in pumping pure sand in the Chance classifiers.

In the gravel boats there is a very different situation; every so often their pumps bring up a stone as big as one's head, and these chilled irons are too brittle to risk in service of that sort. So we who are wrestling with the problem of producing castings to resist pure abrasion are being driven over in some of our work to other materials, and we are forced at times to use steels, hardened by regular heat-treatment methods. We much prefer, whenever possible, to use these nickel-chromium hard irons because when they come out of the sand we are through; if they are not cracked, and they generally are not, we are all right, as they do not require heat treatment. Hardening a complicated steel pump casting either in water or oil, without cracking it, is a difficult matter, and if you use such a composition that air cooling may be resorted to in place of quenching, the castings are very "tender" in the foundry. There are many cases, however, where hardened steels are going to be the only possible solution.

The third line being followed, as we all know, is hard surfacing. Mr. Vanick says that a sand blast nozzle of nickel-chromium cast iron gives five to six times the life of a sand blast nozzle of plain chilled iron, and that is true. But the plain chilled iron nozzle lasts only about five hours, so that a nickel-chromium cast iron nozzle will last only 25 hr. In contrast to this, there are nozzles in use today made with some of the new hard surfacing materials, that will last 25 weeks. There is no particular doubt in my mind that in many cases the solution of the engineer's problem with pure abrasion will be found in the use of hard-surfaced materials, difficult as it is in some cases to apply them.

The problem is being attacked along these three lines: the development of these hard irons, the development of the hardened steels, and the development of hard surface materials. So far we are glad to say that there are a great many applications for which we believe we are going to continue to make these hard irons, which certainly have their place.

R. M. ALLEN, Bloomfield, N. J.—I do not feel that I can add to the data in the paper. Of course, if it had been elaborated a little more along the lines of the questions that Dr. Hall has brought up, it might have been a little more clear to some. This material has a very wide range of structure and it can actually be made very tough, as cast irons go. This reference to the qualifying adjective "tough" ought to be considered with the whole sentence, in the light of what it is that is being described. It is tough *chilled cast iron*. I do not think we should attempt to compare tough

chilled cast iron with tough steel. The thought in this case is that the matrix can be made very tough and the chill can be made very hard as compared to ordinary chilled cast iron.

There are two or three little points in regard to the paper that I think might be brought out. In the first place, in regard to terminology, both in describing the micrographs on page 62 and also in the text on page 61, Mr. Vanick refers, as is common—at least among gray-iron producers—to the pearlitic portion as the matrix.

Of course, in referring to gray irons, the pearlite is logically and properly called the matrix, but to be strictly accurate when we are talking about chilled iron, we have to reverse the terminology. That is, the matrix in this case is not the pearlitic portion. The pearlite, more properly called the dendrites, is the crystalline material that first separates from the molten magma; and the matrix, the last material to solidify and surround the dendrites, is therefore the cementite.

If you look at it in that light, you will see then it is consistent with other metallurgical and mineralogical terms. Those in the mining industry will appreciate that when you find a crystal of any kind lying in a matrix, it is always presupposed that the crystal material is idiomorphic or first formed with reference to the material last formed, and in the case of the chilled iron, the matrix is that which is formed last, the dendrites being the crystals which come out first.

I mention this because I want to be clearly understood in regard to my comments as to the cause of the hardness of this material.

Mr. Vanick has referred to this iron in terms of the hardness of ordinary chilled cast iron; while he has given rather wide ranges of figures, both in wear test and in Brinell, unfortunately those figures do not tell the whole story.

I believe even among metallurgists it is ordinarily conceived that chilled iron is of one grade only and that the hardness is proportionate in a large degree to the depth of the chill. This is a mistaken idea, and so we have a suitable yardstick in order to measure by. I have seen chills  $\frac{1}{4}$  in. deep which in actual wear test under service conditions, in mine car wheels, for instance, or large freight car wheels, wore twice as long as a chill  $\frac{3}{4}$  in. deep on another wheel.

Given an identical chill in composition and method of producing, obviously the deeper the chill, the harder it is at the surface because the chill is progressively softer as you get in away from the surface, but chills produced under different conditions and with different analyses cannot be compared directly by measuring the depth of chill.

In connection with the production of especially hard ordinary chills, I found some years ago that the composition of the iron is very important. The casting temperature also enters into it, and the pouring temperature, and taking it all in all, every factor is very critical. However, in the case of the most wear-resisting and the hardest chill possible without the use of alloys, the Brinell hardness as ordinarily measured steps up from the ranges that Mr. Vanick has given in his paper (for ordinary chilled iron), until I succeeded in producing chills without the use of any alloying elements other than those ordinarily present in car-wheel iron, to practically 700 Brinell, or, in other words, to the range he gives for this superhard iron.

Consequently, when Dr. Merica sent me a sample of one of the first chill blocks I believe they had produced of this new iron, and told me how hard it was and that the structure of it was martensitic, I measured it on the Brinell machine and obtained a Brinell hardness of 750. I was rather disappointed because I thought it should be much harder than that.

It was not until I succeeded in obtaining a Monotron hardness tester and made a diamond Brinell hardness test that I found the real hardness in terms translatable from the one to the other. Dr. Merica's sample, measured  $\frac{1}{8}$  in. below the chilled surface on a ground and polished specimen, ran over 1100 Brinell. The reason for it was obvious when we came to look at the balls after one test on the Brinell machine. They

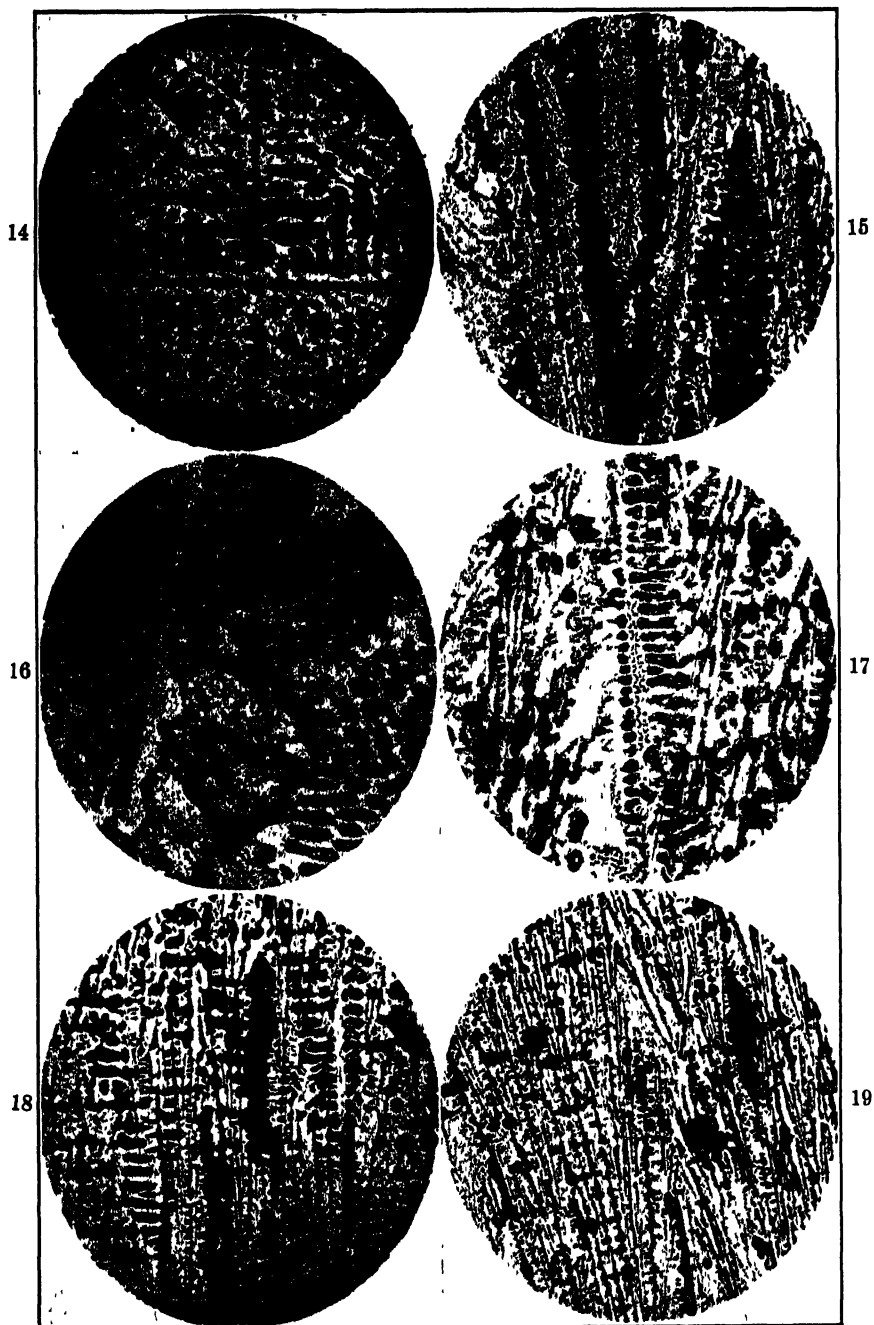


FIG. 14.—WHITE PIG IRON, SHOWING DENDRITES IN A MATRIX OF CEMENTITE.  $\times 175$ .  
 FIG. 15.—CHILLED IRON WITH EQUAL PERCENTAGES OF SILICON AND MANGANESE,  
 SHOWING PRIMARY DENDRITES AND LEDEBURITE EUTECTIC.  $\times 200$ .

become flattened in testing this material, so that the material is really harder than the hardened steel ball used for indenting in the Brinell machine. I think this fact ought to be recognized in talking about this material, or interpreting the figures given by Mr. Vanick.

On the other hand, this material can be made with a much lower Brinell and runs down to the actual figures which Mr. Vanick has given. The interesting work that I did in connection with this was in ascertaining as far as possible wherein the increase in the hardness came.

In various samples which I tested, the microcharacter relative hardness of the cementite to the dendrites ranged over a quite wide area in the Ni-hard samples, running, as I recall, from about  $2\frac{1}{2}$  to 1 in microcharacter hardness terms, to perhaps  $5\frac{1}{2}$  or 6 to 1. That is, the hardness of the cementite ran to about 13,000, the highest figure, and the corresponding figure for the dendrite was perhaps 4500 down to 1500 for dendrites, and perhaps 5000 or 6000 for the cementite. That latter figure is within the range of the best irons which can be produced from the hardness and wear standpoint of the ordinary, unalloyed chilled irons. They average about 5 to 1.

Fig. 14 illustrates the point I wish to make regarding terminology. This is an ordinary white iron, and while we call these black areas the dendrites, you will observe that they are developing into a cubic crystalline structure and look like little pine trees. In this case the dendrites, of course, form first and then as the material falls to a certain temperature all the rest of the material which has been fluid solidifies around it. That is the reason I like to call the pearlitic portion the dendrite and the surrounding material the matrix, which is exactly opposite to the terminology used for gray iron.

Mr. Vanick mentions the effects of manganese. Manganese has a very important role to play in ordinary chilled iron. I think it is from one standpoint more critical even than sulfur. If you strike a certain balance with manganese and silicon—for ordinary chilled irons—that is, an approximately equal ratio regardless of whether it is a 0.50 per cent silicon and 0.50 per cent manganese, 0.80—0.80, or 1.20—1.20—you get the poorest possible chill combination. You then get a perfect development of the so-called Ledeburite eutectic (see Fig. 15, showing a chilled iron having 1.20 per cent silicon and 1.20 per cent manganese).

The suppression of this Ledeburite eutectic, I believe, is one of the important things in developing an ordinary chilled iron so as to produce the maximum hardness.

Fig. 16 shows the same iron at higher magnification, the primary dendrite, graphite coming out within it and the Ledeburite eutectic. As Mr. Vanick pointed out, the dendrites are pearlitic in the ordinary chilled irons. This iron is pearlitic, of course, in the dendrites, whereas in the case of the improved iron under discussion, these are not pearlitic, but range all the way from sorbitic to martensitic.

Fig. 17 shows a much better chill. The Ledeburite eutectic is almost suppressed. There is a little here and there.

Figs. 18 to 21 are all taken from actual samples made for car-wheel purposes and you can see the wide variation that is possible in commercial chilled irons. The wide

FIG. 16.—SAME CHILLED IRON AS OF FIG. 15, AT HIGH MAGNIFICATION, SHOWING PEARLITE AND GRAPHITE IN THE PRIMARY DENDRITE AND THE LEDEBURITE EUTECTIC.  $\times 1750$ .

FIG. 17.—CHILLED WHITE IRON WITH CONSIDERABLE SUPPRESSION OF THE LEDEBURITE EUTECTIC.  $\times 200$ .

FIG. 18.—CHILLED IRON; LARGE DENDRITES BUT LOW PERCENTAGE OF LEDEBURITE, AND LITTLE GRAPHITE.  $\times 200$ .

FIG. 19.—CHILLED IRON; VERY FINE DENDRITES, LOW PERCENTAGE OF GRAPHITE, BUT ABUNDANT LEDEBURITE.  $\times 200$ .

(All figures reduced 50 per cent. Original magnifications given.)



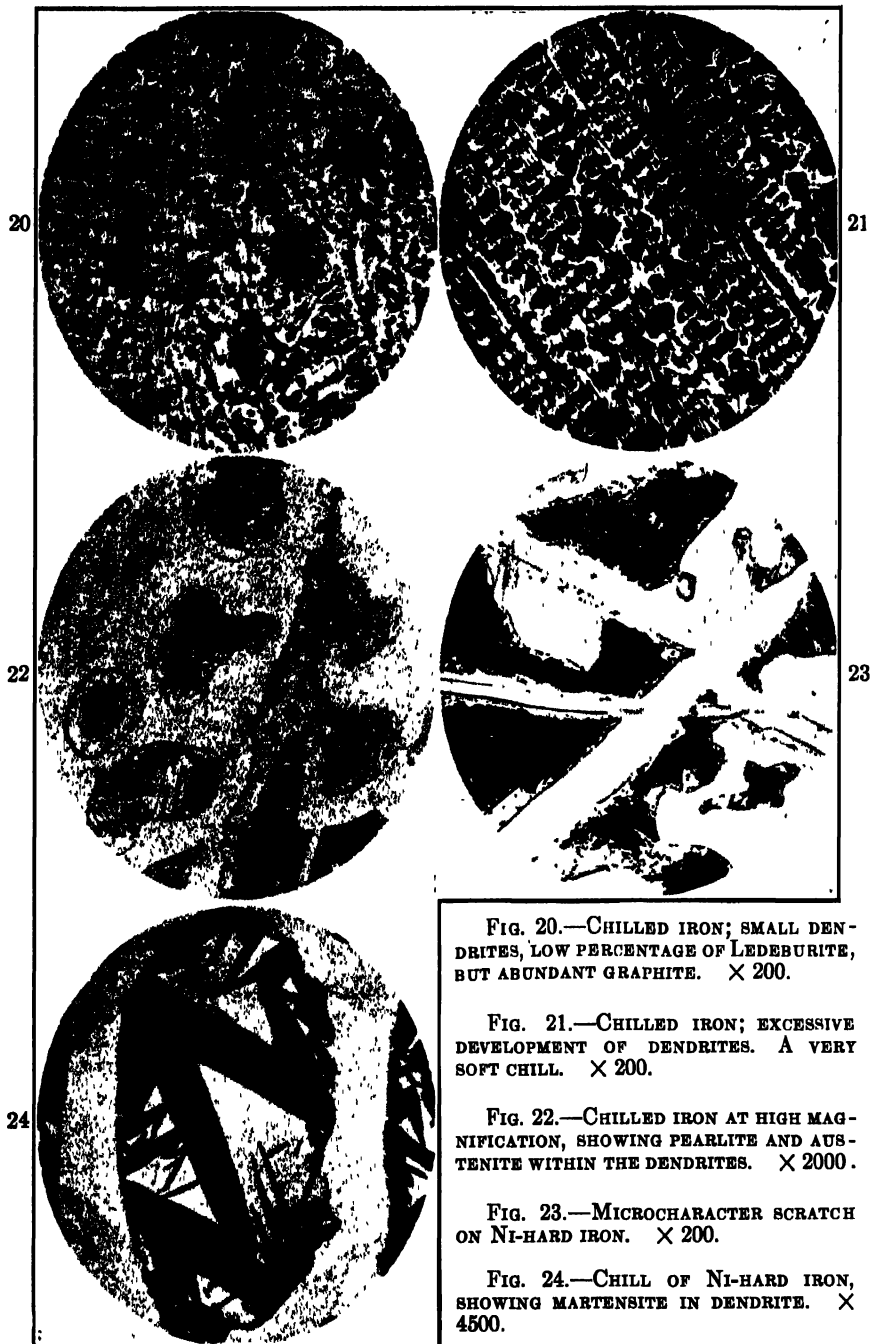


FIG. 20.—CHILLED IRON; SMALL DENDRITES, LOW PERCENTAGE OF LEDEBURITE, BUT ABUNDANT GRAPHITE.  $\times 200$ .

FIG. 21.—CHILLED IRON; EXCESSIVE DEVELOPMENT OF DENDRITES. A VERY SOFT CHILL.  $\times 200$ .

FIG. 22.—CHILLED IRON AT HIGH MAGNIFICATION, SHOWING PEARLITE AND AUSTENITE WITHIN THE DENDRITES.  $\times 2000$ .

FIG. 23.—MICROCHARACTER SCRATCH ON NI-HARD IRON.  $\times 200$ .

FIG. 24.—CHILL OF NI-HARD IRON, SHOWING MARTENSITE IN DENDRITE.  $\times 4500$ .

(All figures reduced 50 per cent. Original magnifications given.)

range in the size of the dendrites, the ratio of dendritic material to cementite and amount of graphite present in the chill should be noted.

Fig. 22 is an enlarged view that I think will serve the purpose Mr. Vanick had in mind in pointing out the presence of the pearlite in these dendrites. Incidentally, this was taken from one that was relatively hard, and you will notice that there is only a partial pearlitic development. Actually, by other methods of etching it can be demonstrated that part of the dendrites is still austenitic.

Fig. 23 will serve to show the effect of a microcharacter scratch. As the diamond passes over the cementite, it develops a certain width and the instant it enters or leaves the dendrites, you find it widens out correspondingly, showing that the soft portions are the dendrites and the hard portions are the clear cementite material. This photograph is from one of the softer grades of Ni-hard iron.

The microcharacter formula is  $K = \lambda^{-2} \times 10^4$  ( $\lambda$  = scratch width in microns), as I recall it, which makes the value go up much faster than would appear in actual scratch width.

With martensitic iron, the dendrites and even the Ledeburite eutectic nodules are equivalent to a perfect martensitic steel base, as may be seen in Fig. 24. As a matter of fact this is a very small spot, as the magnification is 4500.

I believe the real reason why the martensitic or Ni-hard iron under discussion is so much harder is that, first of all, the cementite is hardened, owing to the presence of chromium carbide probably in solution, and then the presence of martensite, troostite, or, at least, sorbite, in the material which runs the nearest to ordinary gray iron. You have your choice in the type of dendrite material, as it is possible to produce at will any of the three. The ideal iron for surface hardness, I think Mr. Vanick will bear me out in this, appears to be that iron in which there is the least difference of microcharacter hardness between the dendrites and the cementite. If the cementite were only about  $2\frac{1}{2}$  times as hard as the dendrites, you would get your maximum wear, whereas when it runs five or six times as hard, you get the poorest conditions as regards hardness and wear.

B. STOUGHTON, Bethlehem, Pa.—Mr. Vanick said he would tell us why the hardness went down after the chromium and nickel reached a certain point. I believe it is a very interesting point.

J. S. VANICK—The decline in hardness—above a certain alloy content, illustrated in one or two of the curves shown, is due to the formation of austenite in considerable quantity in what Mr. Allen likes to call the dendrites.

I think there is considerable history in the making, on the comparison of this type of material against a number of the roll compositions. Unless some of the rollmakers are here, I believe we would prefer to leave that discussion to them. We hope that in the course of a reasonably short time a manuscript dealing with roll production only will be prepared.

J. S. VANICK (written discussion).—The discussion has been so thorough that little remains to be added. If certain details had not been omitted in the initial text, in the interest of brevity, this concluding comment might not have been necessary. Mr. Harding might not have been misled in the matter of an increase in hardness behind the chill for an iron of lower carbon content. The lower carbon iron is much more likely to remain in a mottled condition behind the chill, while its equally alloyed higher carbon companion was more thoroughly graphitized and, therefore, softer. In the text these details are not adequately described. In connection with Mr. Allen's comments, the Brinell hardness testing methods were used as a measure of hardness largely for the reason that the test subjects a larger area of metal to pressure under the ball than is the case with other test methods, and since the structure is composed of

components not necessarily all of the same hardness, a better average picture of about what you are going to get in the way of resistance to deformation is obtained. It is quite possible that in many cases the capacity of the Brinell test was exceeded, although all precautions were taken to use a specially hardened Brinell ball within the range of 750 Brinell and discard the ball after each test. Mr. Allen's scratch test results were certainly valuable in analyzing the hardness of the components of the chilled iron structure and useful in indicating means for providing uniformity or divergence in hardness between structural components as might be desired.

In conclusion, the author wishes to express his thanks to the participants in the discussion for the encouragement and stimulation which their comments aroused.

# Properties of Low-carbon Medium-chromium Steels of the Air-hardening Type

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(New York Meeting, February, 1933)

THIS paper describes some properties of steels in the composition range 0.10 to 0.30 per cent carbon and 1 to 7 per cent chromium. It is well known that some steels of this type develop high tensile strengths upon receiving comparatively simple heat treatments, such as ordinary air cooling from appropriate temperatures, with or without subsequent tempering treatments. These high strengths are frequently associated with unusual toughness as measured by the Izod or Charpy impact test. The chromium content, in addition to imparting the above properties, enhances the resistance to corrosion and improves the strength and oxidation resistance at elevated temperatures. Moreover, these steels have good forging and fabricating properties, as evidenced by the fact that several thousand tons of seamless tubing have been made during the past five years from steels containing 0.10 to 0.25 per cent carbon and 5 per cent chromium.

## COMPOSITION AND PROPERTIES OF MATERIALS TESTED

Twelve 15-lb. induction furnace heats of the compositions shown in Table 1 were prepared, using low-carbon open-hearth steel base melts

TABLE 1.—*Analyses of Steels Melted*

Steel No.	Carbon, Per Cent	Chromium, Per Cent	Manganese, Per Cent	Silicon, Per Cent	Sulfur, Per Cent	Phosphorus, Per Cent
DN	0.100	0.99	0.39	0.17	0.034	0.009
DO	0.108	3.15	0.42	0.30	0.030	0.009
DP	0.099	5.21	0.50	0.34	0.039	0.008
DQ	0.103	7.20	0.46	0.32	0.043	0.006
DR	0.200	0.97	0.38	0.19	0.031	0.012
DS	0.191	3.04	0.45	0.28	0.030	0.007
DT	0.207	5.19	0.51	0.35	0.042	0.009
DU	0.201	7.18	0.52	0.30	0.045	0.006
DV	0.310	1.06	0.42	0.26	0.031	0.010
DW	0.299	3.14	0.52	0.27	0.034	0.009
DX	0.301	5.27	0.39	0.28	0.042	0.008
DY	0.299	7.26	0.54	0.33	0.042	0.008

\* Metallurgist, National Tube Co.

and adding ferroalloys to produce the desired analyses. These heats were cast into ingots 2 in. square and subsequently forged under a steam hammer into 0.675-in. diameter round bars. The nominal analyses of these steels are 0.10, 0.20 and 0.30 per cent carbon, each carbon content being associated with 1, 3, 5 and 7 per cent chromium.

### FORGEABILITY

The term forgeability is considered to embrace those properties of a metal that permit it to be deformed hot without developing cracks or other harmful defects, as well as its rigidity or resistance to such hot deformation. Using initial forging temperatures of 1150° to 1175° C., none of the present steels showed evidence of hot-shortness or the development of surface checks or other defects. In general, increasing either the carbon or the chromium content increased the resistance to hot deformation. In the opinion of the experienced blacksmith who carried out the forging, all of the 0.10 and 0.20 per cent carbon steels, and the 0.30 per cent carbon steels containing 1 or 3 per cent chromium, forged in about the same manner as plain carbon steels containing 0.25 to 0.55 per cent carbon. The 0.30 per cent carbon steels containing 5 and 7 per cent chromium were appreciably harder, forging somewhat like the higher carbon or alloy tool steels.

### TEST SCHEDULE, SPECIMENS, AND PROCEDURE

The procedure in the investigation was to determine by means of Brinell, tensile, and impact tests, and thermal critical point determinations, an appropriate air-hardening temperature for each steel. Following this, tensile and impact tests were made on each steel (1) as air-hardened, (2) as air-hardened and tempered, and (3) as soft-annealed by furnace cooling. The latter tests were included to cover the uses where corrosion or high-temperature oxidation resistance combined with toughness and relative ease of fabrication are the principal requirements.

The tension tests were made using  $\frac{1}{2}$ -in. diameter by 2-in. gage length, threaded-end, cylindrical specimens. Yield points were taken with a Ewing extensometer as the loads required to produce 0.5 per cent (0.010 in.) elongations of the 2-in. gage lengths while under load. With the exception of the three steels containing only 1 per cent chromium and a few of the highly tempered or soft-annealed steels containing 3 per cent chromium, these materials showed continuous increases of both load and extension until the maximum values were reached. With the exceptions noted, the yield points were of the conventional type, showing small, but unmistakable, decreases in the loads at the recorded values.

The impact tests were made using the National Tube Co. combination Izod and Charpy specimen. This is a 0.394 by 0.394-in. square bar, having for the Izod test a 0.01-in. root-radius V-notch 0.079 in. deep, a striking distance of 0.866 in., and a free length of 1.10 in.; for the Charpy

test a No. 47 drill keyhole notch 0.197 in. deep, a beam span of 1.575 in., and a length of 2.165 in. All specimens were tested on a 120 ft.-lb. combination Izod and Charpy machine.

The air-hardening and tempering heat treatments were made on short lengths of the round bar stock prior to machining out the test specimens. The treatment in each case consisted of holding at heat 30 min., and cooling in still air with the bars standing on end. The 30-min. "at-heat" period selected for these steels was considered a reasonable and commercially practicable time for heat-treating operations on tonnage products.

#### SELECTION OF THE AIR-HARDENING TEMPERATURES

The selection of an appropriate air-hardening temperature for each steel was considered an important phase of this investigation. It was known that at least those compositions containing upwards of 3 per cent chromium would harden upon simply cooling naturally in still air from a wide range of temperatures having a minimum somewhere around 800° C. This hardening is of an intense order; being comparable, in fact, to that obtained with most high-strength structural steels only by quenching in a liquid medium.

The basis for the selection of the most appropriate air-hardening temperature was that of the numerous combinations of air-hardening and drawing temperatures which might be used to develop a certain required tensile strength, the "best" combination is that for which the required strength has associated with it the highest toughness, meaning by the latter term the property measured by the notched-bar impact tests. The experimental procedure therefore consisted of air-hardening samples of each steel from a number of temperatures; tempering these samples at individually selected temperatures so as to bring all samples of a given steel to very closely the same final strength; and then by means of Izod and Charpy tests determining which treatment had developed the highest toughness.

A general survey of the behavior of these steels during heat treatment was first made by a series of 300 Brinell tests. Here groups of five small cylindrical specimens of each steel were air-hardened from each of the temperatures 800°, 825°, 850°, 875° and 900° C., one specimen from each group being tested as air-hardened and the remaining four after being drawn one each at the temperatures 450°, 550°, 650° and 750° C. A study of the resulting data revealed that the hardness after each drawing treatment increased progressively with the air-hardening temperature, and that 800° C. was too low a temperature to produce satisfactory results. The tension and impact test samples were accordingly air-hardened only from 825°, 850°, 875° and 900° C. The drawing temperatures to be used with each of these air-hardening temperatures, in order to develop the same final Brinell hardness (tensile strength) with the four samples from a given steel, were found by reading off the intercepts of a "constant-

hardness line" with the four curves obtained by plotting the Brinell versus drawing temperature values determined in the preliminary investigation. For each steel the "constant-hardness line" was placed so that the four drawing temperatures had a mean value of about 650° C.

In many cases the changes in impact strength with air-hardening temperature were not as marked as had been anticipated, and in a few instances the tensile strengths of the four samples from a given steel were not as uniform as had been desired. However, after allowing reasonable adjustments and paying some attention to the systematic arrangement of analyses of the materials being studied, the data indicated that the highest toughness would be obtained by air-hardening steels DN and DO (0.10 per cent carbon, 1 and 3 per cent chromium) at 900° C., and all the remaining compositions at 875° C. As a matter of fact, variations of 25° C. above or below the selected air-hardening temperatures do not cause changes of any importance in the final results. This may be considered an advantage from a manufacturing standpoint, since it will allow considerable latitude in this step of the heat-treating operation.

Thermal analyses of the 12 steels verified the correctness of the conclusions drawn from the results of the physical tests. These critical point determinations were made by the differential method using a neutral body of pure nickel. In the higher carbon and higher chromium alloys the definite location of the critical points was somewhat obscure, in some instances the several points being merged into a single thermal disturbance. For practical purposes in heat-treating the end of the thermal critical range upon heating is the essential information. This is given in Table 2.

TABLE 2.—*Thermal Analysis Data*

Steel (1)	Chemical Analysis		Air-hardening Temperature Selected by Physical Tests, Deg. C. (4)	End of Critical Range on Heating, Deg. C (5)
	(2)	(3)		
DN	0.100	0.99	900	869
DO	0.108	3 15	900	857
DP	0.099	5 21	875	835
DQ	0.103	7 20	875	832
DR	0.200	0.97	875	841
DS	0.191	3.04	875	837
DT	0.207	5.19	875	832
DU	0.201	7.18	875	835
DV	0 310	1 06	875	823
DW	0.299	3.14	875	823
DX	0.301	5.27	875	834
DY	0.299	7.26	875	832

Comparison of columns 4 and 5 in this tabulation shows that the selected air-hardening temperatures are from 30° to 50° C. above the ends of the critical ranges during heating. This relationship is in conformity with the commonly accepted principles of heat treatment.

#### DISCUSSION OF DATA ON PHYSICAL PROPERTIES

Using the air-hardening temperatures determined by the preliminary experiments, samples of each steel were given various heat treatments, and were then tested in tension and impact. These tests included specimens as air-hardened, others as air-hardened and drawn at approximately 50° C. intervals in the range 550° to 750° C., and finally specimens furnace-cooled from the same temperature used for air-hardening. The complete results of these tests are given in Table 3.

These data show clearly the reactions of the various steels to heat treatments and the effects of changes in the carbon or chromium content upon the physical properties. No lengthy discussion of them will be given, but among the main points to be noted is that most of these steels respond to the simple air-hardening (air-quenching) treatments in the same manner as do most of the higher strength structural steels to liquid quenching. With suitable amounts of chromium, the strengths in the air-hardened condition are very high, while ductility and toughness are at a correspondingly lower level. Upon tempering, the strength is reduced, while ductility and toughness are greatly improved. For maximum toughness, drawing temperatures of 600° to 650° C. or higher are required.

Steels containing 1 per cent chromium show only very slight air-hardening ability, even with carbon contents as high as 0.30 per cent. Steels containing 0.20 or 0.30 per cent carbon require about 3 per cent chromium, and those containing 0.10 per cent carbon require about 5 per cent chromium in order to attain the maximum air-hardening ability. For a given condition of heat treatment—*i. e.*, fixed drawing temperature—raising the chromium content above these levels (at least up to 7 per cent) is not justified by the further slight changes in physical properties thereby obtained. If the higher amounts of chromium are used in order to obtain corrosion resistance, or for other reasons, higher drawing temperatures may be used and this will result in improved ductility and toughness with no loss of strength. With the lower chromium content, increasing the carbon from 0.10 to 0.30 per cent has quite a pronounced effect on the toughness, but it will be noted that even with 0.30 per cent carbon the toughness is probably sufficient for all present and near-future requirements. It seems likely that for services in which strength is the primary consideration steels containing about 0.30 per cent carbon and 3 per cent chromium would be used, since this would not only reduce the total amount of chromium required but also would permit



TABLE 3.—*Tensile and Impact Properties of Chromium Steels after Various Heat Treatments*

Steel	Chemical Analysis		Heat Treatment		Tensile Properties				Impact	
	Carbon, Percent	Chromium, Percent	Air Hardening Temp., Deg.C.	Drawing Temp., Deg.C.	Yield Point, Lb./Sq. In.	Tensile Strength, Lb./Sq. In.	Elong. Over 2", Percent	Red. of Area, Percent	Isot. Charpy, Ft.-Lb.	Charpy, Ft.-Lb.
1M	0.100	0.99	900	Not drawn	44,410	60,000	41.5	75.4	88.2	68.9
1M	0.100	0.99	900	750	44,050	59,190	42.5	76.0	86.6	59.6
1M	0.100	0.99	900	607	42,000	56,150	42.5	75.9	87.6	64.4
1M	0.100	0.99	900	665	40,630	57,850	42.0	77.6	86.3	60.5
1M	0.100	0.99	900	700	40,240	56,770	44.0	76.9	87.4	69.4
1M	0.100	0.99	900	750	39,150	57,110	43.0	77.5	86.5	64.6
1M	0.100	0.99	900	Furnace Cool	38,590	55,850	43.0	77.5	87.7	60.0
20	0.108	3.15	900	Not drawn	60,370	102,380	19.0	49.1	85.6	84.8
20	0.108	3.15	900	750	76,460	112,900	16.0	51.6	84.8	86.8
20	0.108	3.15	900	607	68,880	88,110	25.0	72.3	85.4	40.8
20	0.108	3.15	900	650	58,870	80,410	26.0	76.8	90.1	51.8
20	0.108	3.15	900	689	55,480	76,580	30.0	77.7	90.3	68.5
20	0.108	3.15	900	750	47,850	70,090	35.0	77.7	100.7	74.6
20	0.108	3.15	900	Furnace Cool	35,670	60,840	40.0	76.2	88.4	57.5
1P	0.099	5.21	875	Not drawn	108,860	181,420	15.5	53.2	87.3	18.5
1P	0.099	5.21	875	750	186,890	169,480	16.5	57.4	81.1	19.1
1P	0.099	5.21	875	607	102,180	114,100	20.0	71.0	76.4	44.9
1P	0.099	5.21	875	650	86,960	100,100	23.0	73.2	90.4	51.2
1P	0.099	5.21	875	700	76,510	91,810	25.0	76.2	102.6	55.6
1P	0.099	5.21	875	750	67,850	84,810	27.5	77.9	100.5	60.4
1P	0.099	5.21	875	Furnace Cool	27,500	66,050	37.5	75.4	76.8	47.0
1Q	0.105	7.80	875	Not drawn	111,640	192,040	15.0	42.7	80.2	21.0
1Q	0.105	7.80	875	750	180,890	180,350	16.0	54.3	19.4	19.3
1Q	0.105	7.80	875	607	102,870	117,110	20.0	66.0	68.5	41.2
1Q	0.105	7.80	875	650	90,350	105,810	21.5	70.8	89.5	49.5
1Q	0.105	7.80	875	700	79,830	95,790	24.0	74.1	98.9	51.2
1Q	0.105	7.80	875	750	65,000	87,870	26.0	77.3	101.0	56.8
1Q	0.105	7.80	875	Furnace Cool	26,980	67,670	37.0	74.8	90.5	66.6
1R	0.200	0.97	875	Not drawn	50,880	73,000	35.0	68.9	76.9	47.8
1R	0.200	0.97	875	750	50,180	72,520	36.5	69.2	77.4	47.1
1R	0.200	0.97	875	607	50,050	71,540	37.5	68.8	76.2	46.2
1R	0.200	0.97	875	675	48,130	70,090	36.0	67.1	81.8	49.4
1R	0.200	0.97	875	700	46,900	68,580	37.5	70.2	80.6	51.0
1R	0.200	0.97	875	750	45,280	66,780	38.0	70.9	85.2	52.1
1R	0.200	0.97	875	Furnace Cool	36,560	66,840	35.5	60.6	64.6	41.0
1S	0.191	3.04	875	Not drawn	102,380	168,470	15.5	40.5	13.8	12.4
1S	0.191	3.04	875	750	117,450	157,690	16.0	50.8	15.6	12.5
1S	0.191	3.04	875	607	114,210	134,810	19.0	60.4	32.8	25.5
1S	0.191	3.04	875	665	87,130	104,150	24.0	68.9	49.5	47.5
1S	0.191	3.04	875	700	74,900	95,600	26.0	71.7	100.4	56.5
1S	0.191	3.04	875	750	64,640	84,750	26.0	73.9	101.0	57.5
1S	0.191	3.04	875	Furnace Cool	26,170	72,080	34.0	75.6	66.6	42.9
1T	0.207	5.19	875	Not drawn	113,950	212,310	9.0	18.5	25.4	15.6
1T	0.207	5.19	875	750	137,970	194,840	14.5	46.6	16.6	12.5
1T	0.207	5.19	875	607	119,870	137,560	18.5	58.7	35.7	39.0
1T	0.207	5.19	875	650	95,090	115,440	22.5	69.4	81.6	45.7
1T	0.207	5.19	875	700	85,420	104,720	25.0	68.0	85.9	54.4
1T	0.207	5.19	875	750	72,040	95,840	27.5	71.5	86.2	57.4
1T	0.207	5.19	875	800	60,750	94,640	29.0	70.2	81.7	58.4
1T	0.207	5.19	875	Furnace Cool	32,850	75,670	32.0	75.0	81.1	66.6
1U	0.201	7.18	875	Not drawn	119,450	222,370	10.0	22.8	19.4	16.0
1U	0.201	7.18	875	750	137,420	209,500	14.0	45.6	17.7	15.4
1U	0.201	7.18	875	607	105,470	125,510	20.0	61.1	75.4	36.5
1U	0.201	7.18	875	650	95,500	114,040	22.0	69.0	80.5	44.6
1U	0.201	7.18	875	700	82,950	105,480	24.0	70.9	87.9	49.4
1U	0.201	7.18	875	750	72,550	96,960	27.5	73.0	97.0	52.7
1U	0.201	7.18	875	Furnace Cool	35,750	79,210	35.0	76.5	104.1	61.5
1V	0.310	1.06	875	Not drawn	62,680	97,860	24.5	60.5	42.3	38.0
1V	0.310	1.06	875	750	60,140	96,750	26.0	60.0	40.0	39.1
1V	0.310	1.06	875	607	57,980	94,650	26.5	60.4	42.5	31.0
1V	0.310	1.06	875	650	56,570	93,060	27.0	60.1	41.2	32.6
1V	0.310	1.06	875	689	54,590	91,840	28.0	61.9	59.2	31.7
1V	0.310	1.06	875	750	54,080	88,350	30.5	65.6	54.0	36.4
1V	0.310	1.06	875	Furnace Cool	45,510	81,800	26.0	46.9	39.6	19.0
1W	0.299	3.14	875	Not drawn	116,570	207,450	10.5	26.6	19.3	16.3
1W	0.299	3.14	875	750	137,700	194,190	16.0	48.7	15.0	15.2
1W	0.299	3.14	875	607	117,180	136,960	19.0	59.6	50.9	30.1
1W	0.299	3.14	875	650	100,710	127,050	22.0	67.4	66.7	37.4
1W	0.299	3.14	875	700	88,160	108,440	25.5	70.8	87.6	47.1
1W	0.299	3.14	875	750	75,070	96,350	27.0	72.2	94.9	53.2
1W	0.299	3.14	875	Furnace Cool	57,850	87,470	30.0	65.6	12.0	28.4
1X	0.301	5.27	875	Not drawn	117,860	221,850	13.5	31.7	16.9	15.4
1X	0.301	5.27	875	750	143,300	195,570	14.5	48.8	17.2	15.1
1X	0.301	5.27	875	607	116,840	137,400	18.0	60.5	59.1	35.6
1X	0.301	5.27	875	650	97,040	120,220	21.0	66.7	76.5	41.4
1X	0.301	5.27	875	700	85,020	108,080	24.0	69.6	89.1	46.9
1X	0.301	5.27	875	750	75,280	99,700	26.0	72.0	97.0	60.6
1X	0.301	5.27	875	800	69,610	96,750	30.0	74.1	78.5	55.6
1X	0.301	5.27	875	Furnace Cool	38,420	70,590	35.5	75.6	79.9	79.4
1Y	0.299	7.26	875	Not drawn	122,760	235,560	12.5	35.4	16.6	9.6
1Y	0.299	7.26	875	750	144,840	195,300	15.0	41.6	15.0	15.0
1Y	0.299	7.26	875	607	113,560	135,570	19.0	58.6	61.6	32.1
1Y	0.299	7.26	875	650	96,550	125,190	21.0	66.7	61.7	39.9
1Y	0.299	7.26	875	700	85,220	111,950	24.5	69.1	84.7	52.6
1Y	0.299	7.26	875	750	76,320	104,220	27.5	70.6	91.9	60.2
1Y	0.299	7.26	875	Furnace Cool	57,870	84,650	33.5	75.3	90.4	80.3

the use of the higher carbon (and thereby less expensive) grades of ferrochrome in making the steel.

### RESISTANCE TO CORROSION

To determine the relative corrodibility of low-carbon steels with chromium contents up to 7 per cent, an additional series of steels produced in the same manner as those discussed above, and containing 0.15 per cent carbon, were subjected to corrosion tests in five different media for 30-day periods. For comparison, there was included in this series one steel without chromium.

For each material, three specimens 0.670-in. diameter by  $1\frac{1}{4}$  in. long were exposed to the action of four corrosive solutions at room temperature, contained in separate units of a standardized corrosion-test apparatus, and to the action of aerated Pittsburgh city water at  $140^{\circ}$  F. flowing through an open tank. In the corrosion-test apparatus, the specimens, properly insulated from each other, were suspended from a planetary gear arrangement that served to rotate and move them through the corroding medium at a fixed rate. Factors such as depth of immersion, volume of solution and rate of influx of air or hydrogen sulfide were under control. The specimens suspended in the open tank of Pittsburgh water were held stationary.

The four solutions were a 3.5 per cent solution of sodium chloride agitated with hydrogen sulfide, an aerated 3.5 per cent solution of sodium chloride, an aerated dilute solution of sulfuric acid and an aerated dilute solution of hydrochloric acid. The strength of each dilute acid solution was maintained at  $\text{pH of } 4.0 \pm 0.4$  by slowly and continuously adding a dilute solution of known strength of the corresponding acid. The volume was held constant by siphoning off the excess solution.

The average results of the corrosion tests are given in Table 4, and show a distinct advantage in favor of the chromium steels. The measure of the pitting attack, shown as the calculated maximum penetration in inches per year, should not be considered as absolute, but only as denoting the trend. Due to disturbing influences that arise in service, it is probably not correct to consider the maximum pitting as a linear function of time. On the other hand, it is approximately correct to consider the average penetration as a function of time, and figures of average penetration in inches per year obtained from 30-day losses are considered reliable and comparative. Study of the corrosion data indicates that, of the alloys included in this investigation, those containing between 3 and 5 per cent chromium show good resistance to attack, and that little is to be gained by further increasing the alloy content to 7 per cent. The benefit derived from the chromium additions is to decrease corrosion damage to one-half or less of that resulting on plain carbon steel under similar conditions.

TABLE 4.—*Corrodibility of Chromium Steels*

Corroding Medium and Test Factor	Chromium Content of Steels, Per Cent				
	0 00	1 06	2 77	4 64	7.14
Aerated, flowing, Pittsburgh city water at 140° F.					
Loss in 30 days, grams per sq. in. . . . .	0.2096	0 3148	0.1033	0 0890	0.1192
Average penetration, in. per year . . . . .	0 01985	0 02988	0.00982	0 00848	0.01139
Maximum penetration, in. per year . . . . .	N.P.	N.P.	0 036	0 080	0 180
Aerated, dilute, hydrochloric acid solution at 70° F.					
Loss in 30 days, grams per sq. in. . . . .	0 2626	0.2341	0 0800	0 0480	0 0393
Average penetration, in. per year . . . . .	0 02487	0 02222	0.00761	0 00458	0.00376
Maximum penetration, in. per year . . . . .	N.P.	N.P.	0 012	0 028	0 060
Aerated, sodium chloride solution at 70°F.					
Loss in 30 days, grams per sq. in. . . . .	0 1249	0 0941	0 0684	0 0757	0 0804
Average penetration, in. per year . . . . .	0 01183	0 00893	0 00651	0 00722	0 00768
Maximum penetration, in. per year . . . . .	N.P.	0 120	N.P.	N.P.	N.P.
Sodium chloride solution agitated with hydrogen sulfide and at 70° F.					
Loss in 30 days, grams per sq. in. . . . .	0 2380	0.1085	0 0526	0 0433	0 0325
Average penetration, in. per year . . . . .	0.02254	0 01030	0 00500	0 00413	0 00311
Maximum penetration, in. per year . . . . .	N.P.	N.P.	N.P.	N.P.	N.P.
Aerated dilute sulfuric acid solution at 70° F.					
Loss in 30 days, grams per sq. in. . . . .	0 2470	0 2141	0 1397	0 1023	0 0763
Average penetration, in. per year . . . . .	0 02340	0 02032	0 01329	0 00975	0 00729
Maximum penetration, in. per year . . . . .	N.P.	N.P.	N.P.	0 012	0 012

N.P. = Not pitted.

## CONCLUSION

The results of this investigation indicate that steels of desirable properties may be obtained from the range of composition and heat treatments studied. It is evident that the 1 per cent chromium series does not contain sufficient chromium to improve either the mechanical properties or corrosion resistance to any marked extent, while the steels containing 7 per cent chromium do not exhibit any particular advantages over those containing 3 and 5 per cent chromium.

Physical properties of the 3 and 5 per cent chromium alloys developed some interesting possibilities. In the first place, these steels can be soft-annealed to develop properties very similar to those of mild carbon steels, and therefore suitable for equipment where severe cold work is applied during fabrication. On the other hand, some steels with remarkably high yield points and tensile strengths, combined with excellent ductility and impact toughness, can be produced by simple air-hardening treatments. It is obvious that many articles of shapes that make

quenching in liquid media difficult might be produced from steels containing either 3 or 5 per cent chromium, and subsequently heat-treated, without excessive distortion, to desired properties. A noticeable feature of these air-hardening alloys is the variation in the elastic ratio; for example, these steels in the air-hardened and untempered condition have ratios of yield point to tensile strength of about 0.50 to 0.55, and even lower proportions in the fully soft-annealed condition. Reheating of the air-hardened steels to various tempering temperatures reduces the tensile strength noticeably, while the yield point is only slightly lowered and elastic ratios of about 0.75 and 0.80 appear in the tempered specimens.

It is believed that the particular properties exhibited by these alloys, as compared to ordinary air-hardening steels, can be associated with their structures. Most of the S.A.E. steels that show air-hardening properties also have a pearlitic structure when soft-annealed. On the other hand, the structures of the 3 and 5 per cent chromium alloys rarely exhibit normal pearlite, the carbides usually being of a globular or coalesced type dispersed throughout the ferrite matrix. It is believed that on hardening and tempering this tendency toward random dispersion of carbides promotes the high tensile properties and also the high impact toughness which pearlitic steels do not develop.

#### ACKNOWLEDGMENTS

The authors wish to extend their thanks to Messrs. J. Jay Dunn, I. B. McCorkle, A. W. Simpson, and other members of National Tube Company's metallurgical staff, who contributed greatly to the execution of this work.

#### DISCUSSION

*(F. N. Speller presiding)*

F. N. SPELLER, Pittsburgh, Pa.—This work by Messrs Wright and Mumma is a compilation of results of experimentation in the research department of the National Tube Co two or three years ago. Recently we have checked the corrosion tests and have gotten practically the same results; that is to say, 3 per cent chromium steel of these types seems to have three times the durability of ordinary steel in a wide variety of water solutions and in resistance of oxidation up to 1100° F., whereas when the chromium content is below 1.5 per cent, it is hardly worth considering for this purpose. This again indicates the improbability of finding low-alloy steel of reasonable cost compared with carbon steel that will show increased durability in water, or in the ground. In soil the chromium content must be increased very considerably before anything like that difference in durability is found. In atmosphere, of course, it takes less of elements such as copper or chromium to show rather marked difference in life.

These steels, as the authors have pointed out, seem to afford a rather wide range of application on account of the wide range of physical properties than can be obtained by various air treatments and also by their substantially better resistance to corrosion.

It is interesting to note that about the same results can be obtained with 3 per cent chromium as with 5 or 6 per cent chromium under the particular conditions we

are talking about, although when applied to other conditions, as in oil-cracking tubes, the difference is perhaps in favor of the high-chromium steels of this series.

A. B. KINZEL, New York, N. Y.—Regarding the applications mentioned by both the authors and Dr. Speller, I might mention that these steels are used not only in oil cracking, etc., but also in fields as far removed from chemicals as railroading, for example. Railroad rails of these steels have been in service for some time with extremely good result. We really have a new type of engineering material in these steels.

P. R. KOSTING, Watertown, Mass.—Have you any information on the behavior of such steel in an alkaline medium?

H. M. GERMAN, New York, N. Y.—The creep value of this steel is of vital importance. It has one of the highest creep values of any steel that has been developed in recent years, and for that reason it is finding extensive applications at the higher temperatures, not only for tubes, but also for bolts and studs. In the last year there has been a definite development not only of the 4 to 6 per cent but also a 4 to 6 per cent chrome steel with the addition of 0.40 to 0.60 per cent molybdenum. This steel is largely supplanting the straight 4 to 6 chromium grade. In the last year the rough figures have been better than 5000 tons of this material produced.

A. B. KINZEL —Mr. Wright will undoubtedly have something to say about the caustic resistance. In the work on this problem done at the Engineering Station of the University of Illinois, of which a report has been published and is available, it was found that the only steels that would fully resist the caustic embrittlement treatment test were the steels with a minimum of 12 per cent chromium and without large austenite-forming alloy additions.

F. N. SPELLER.—It is unfortunate that the voluminous research report on which this paper is based could not have been more fully abstracted. The condensation was made to bring the paper within the limits possible for printing as an Institute publication.

Referring to the question of pitting, it seems to me that this is largely influenced by external environment rather than by the metal itself. In soil, for instance, the high-chromium steels show a certain tendency to pit. Even 18-8 steel shows localized corrosion where it is in contact with material that produces electrolytic cell effects.

Again I would like to point out the significant fact that it takes a considerable amount of these alloying elements to show any very marked improvement in iron when immersed in water, in contact with wet soil or other environment that tends to produce electrolytic effects such as are due to the oxygen concentration cell, or in contact with dissimilar materials.

MEMBER.—Can you define the water a little more closely than "Pittsburgh water"? Can you give the pH of the water?

E. C. WRIGHT.—It runs about 6. The test was run in Pittsburgh water because we are interested in pipe. We were not interested so much in the actual open composition of the water, but the actual test of the pipe where the water and acid flowed for 30 days.

H. STYRI, Philadelphia, Pa.—I would like to have some Brinell hardness figures on these steels.

E. C. WRIGHT.—The hardnesses run for the air-hardened steels up to 450 Brinell. That was the maximum hardness.

Regarding the question about caustic corrosion, the 5 per cent chrome steels have been used, some in sulfate paper mills and evaporators where there is a high caustic content, with very good results. As far as we know, the alkaline solutions do not bother the 4 6 chrome steels, especially if there are oxidizing conditions.

P. R. KOSTING.—What is the tendency to pit under caustic conditions?

E. C. WRIGHT—That tendency is so variable that I cannot answer that question.

We would also be much interested in the creep properties of these steels, although the 5 per cent chromium steels do not show remarkable creep properties unless they have additions of tungsten or molybdenum. So I would not like to say that the 3, 5 and 7 per cent chromes are remarkable for creep. In this investigation we were primarily interested in structural properties of the steel in use at ordinary temperatures

# Hot-hardness of High-speed Steels and Related Alloys\*

BY OSCAR E. HARDER† AND H. A. GROVE,‡ COLUMBUS, OHIO

(New York Meeting, February, 1933)

IT is now just a quarter of a century since Fred W. Taylor§<sup>(23)</sup> published his classical paper *On the Art of Cutting Metals*, describing his researches in which he, in cooperation with Maunsel White, had developed what is essentially the modern method of heat-treating high-speed steels. Regarding this research, Dr. Sauveur,<sup>(22)</sup> in his address on *Steel Wizards, Past and Present*, at the annual banquet of the American Society for Steel Treating in Philadelphia in 1920 said, "The discovery of high-speed steel, or if you prefer, of the treatment imparting high-speed properties to certain steels by Taylor and Maunsel White I am inclined to consider as our one epoch-making contribution to the metallurgy of steel." It was at about that same time (1900) that Taylor exhibited high-speed steels, heat-treated by the improved process, at the World's Exposition in Paris and attracted much attention by showing that the steels would operate at such feeds and speeds that the tips of the tools were visibly red hot. This observation must have started metallurgists to wondering regarding the relative hardness of the various steels at red-heat temperatures.

Considerable work has indeed been done in an effort to measure the hardness of high-speed steels and related materials in the red-heat range, using various methods. The results, however, have been only partly satisfactory, owing to experimental difficulties.

The present investigation had as its immediate inception an address by J. V. Emmons, of the Cleveland Twist Drill Co., to the Columbus Chapter of the American Society for Steel Treating in 1931, in which he deplored the fact that comparatively little was known with regard to the hardness of high-speed steels at elevated temperatures, in spite

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\* The experimental data herein reported are largely from the work of H. A. Grove, who held the Battelle Memorial Institute Fellowship in the Graduate School of Ohio State University during the school year of 1931-1932. Some of the results were submitted by H. A. Grove in a Master's thesis under the advisorship of Prof. D. J. Demorest in the Department of Metallurgy of Ohio State University. The experimental work was done in the laboratories of Battelle Memorial Institute under the direction of H. W. Gillett, Oscar E. Harder and H. W. Russell.

† Assistant Director, Battelle Memorial Institute.

‡ Fellow, Battelle Memorial Institute.

§ The reference numerals in the text refer to the original literature given in the bibliography at the end of this paper.

of the obvious interest and probable importance of such knowledge. Shortly after that Dr. H. W. Gillett proposed that we follow Cowdrey's<sup>(3)</sup> suggestion that the mutual-indentation method of hardness testing might be applied to the determination of the hot-hardness of high-speed steels. This method evaluates hardness on the basis of load divided by area of permanent deformation, just as does the Brinell test, save that two cylindrical specimens in parallel position are pressed together and deform each other instead of the indenter remaining essentially undeformed. The principles underlying the method are the same as those of the Brinell method, and the results may readily be converted into true Brinell figures, as Cowdrey clearly showed. Avoidance of error due to chilling of the indented specimen by a colder ball, or of too great deformation of the ball itself, makes the mutual-indentation method obviously suited to the problem.

A large number of high-speed steels, representing present commercial products, and some related alloys have been secured, heat-treated according to commercial practice, and tested over the temperature range up to 800° C. (1470° F.). In addition to typical high-speed steels, some steels that are used for services that involve high heat, and some nonferrous alloys that are used as high-speed cutting tools, have been studied. Furthermore, a series of tools that had been used at the U. S. Bureau of Standards in various cutting-efficiency tests has been tested through this temperature range in an attempt to find whether any correlation exists between the hot-hardness and cutting efficiencies.

### *Review of Previous Studies*

Three methods have been used in studies of the hardness of metals and alloys at elevated temperatures. These same methods have been used in determining the hot-hardness of high-speed steel.

*Method A.*—The sample to be tested is heated to the desired temperature, removed from the furnace, and then tested in the usual way. Generally the Brinell test has been applied. Obviously the method is open to the criticism that the indenting ball is cold and, therefore, cools the metal at the contact. The specimen cools down during testing, and at higher temperatures the ball may be softened.

*Method B.*—This method determines the impact or drop hardness, and then either expresses the results as the work divided by the volume of the indentation (mm. kg./cu. mm.), or by reference to a curve converts these values into equivalent static hardnesses. This method has been rather extensively used, because the time during which the indenter is exposed to the high temperature is reduced to a minimum. Usually a ball of 5 or 10-mm. diameter has been used as the indenter and the diameter of the impression measured. In some cases a material of known



hardness has been placed back of the ball, so that it also showed an impression as a result of the impact, from which the relative hardnesses can be calculated. This method is open to the objections that the indenter is cold and that impact hardness values may not be directly comparable to static hardness values.

*Method C.*—In this method the indenter and the specimen are both heated to the desired temperature and the test made either by the static or impact method. The advent of the cemented tungsten carbide ball has made it possible to make the ordinary Brinell test at temperatures extending well into the red-heat range. The Monotron instrument using a diamond ball has also been used in this method of testing.

Some of the results which have been obtained by the three different methods of determining hot-hardness are briefly reviewed below, with special attention given to the results obtained on high-speed steels.

*Results of Test by Method A.*—As early as 1905, Brinell<sup>(2)</sup> applied the "ball testing" method to the determination of the relative hot-hardness of low-carbon acid and basic steels. Kürth<sup>(18)</sup>, in 1909, determined the hardness of 0.20, 0.39, 0.51 and 0.75 per cent carbon steels up to temperatures of about 500° C. (930° F.), and later Ito<sup>(15)</sup> determined the hot-hardness of cast iron and steels of different carbon contents.

d'Arcambal<sup>(4)</sup> determined the hardness of six high-speed steels up to 650° C. (1200° F.). His method involved heating disks  $\frac{5}{8}$  in. thick, in an electric furnace, to the desired temperature, placing the disk on a steel block at the same temperature and then making the Brinell hardness test in the usual manner. The diameter of the impression was read immediately after testing and again after the specimen had cooled to room temperature. A new steel ball was used for each test when the testing temperature was 425° C. (800° F.) or higher. The compositions of the steels used and the results obtained at 540°, 595° and 650° C. (1000°, 1100° and 1200° F.) are shown in Table 1.

TABLE 1.—*Hot-hardness of High-speed Steels (d'Arcambal)<sup>a</sup>*

Steel No	Chemical Composition, Per Cent						Hot-hardness, Brinell		
	C	Cr	W	V	Co	Mo	1000° F. 540° C.	1100° F. 595° C.	1200° F. 650° C.
1	0.70	3.53	17.6	0.68			444	418	387
2	0.67	3.66	17.4	0.95			477	418	
5	0.70	4.43			5.25	4.90	460	418	340
6	0.68	3.68	17.5	0.97	3.37		512	444	387
7	0.70	4.45	12.65	1.18			444	418	364
12	0.80	3.57	14.70	1.75			477	418	418

<sup>a</sup> Specimens quenched in oil from 2350° F. and tested as quenched except No. 2, which was tempered at 450° F. (230° C.).

In addition to these tests, specimens of the same steels were heated in a charcoal pack to 2050° F. (1120° C.), quenched in oil, and tested. These specimens were generally lower in hardness.

Regarding these tests, d'Arcambal<sup>(4)</sup> said:

These Brinell tests at high temperature were a little disappointing in the results obtained, as the steel which showed the greatest cutting efficiency (No. 12) did not show a higher Brinell hardness at the different temperatures than some of the other brands. The steel which showed the poorest cutting qualities (No. 5), however, did show lower hardness at elevated temperatures.

It should be noted that the maximum testing temperature used by d'Arcambal was only 650° C. (1200° F.), and yet at that temperature there is beginning to show the superiority of steel No. 12 (hardness 418), which contained higher vanadium, and of No. 6 (hardness 387), which contained cobalt, these steels being rated first and second respectively in the cutting tests.

*Results of Method B.*—This method has been rather extensively used in determining the hot-hardness of high-speed steels and other metals, and the investigators have usually followed the procedure developed by Wüst and Bardenheuer.<sup>(24)</sup> These authors made an extensive study of the relation of the Brinell hardness as determined by the ordinary method and the "drop hardness" or impact hardness of a large number of materials ranging in Brinell hardness from under 100 to values over 700. From their researches they drew a curve to show the relation between the impact and the static Brinell hardness, and this curve has been used in later researches for conversion purposes. They also concluded that there is essentially a straight-line relation between the "drop hardness" of a large number of materials and the tensile strength, in which the relation is essentially the tensile strength equals  $0.193 \times$  the "drop hardness," the tensile strength being expressed in kilograms per square millimeter. Their "drop hardness" is expressed as the product of the height of fall in millimeters times the weight of the ball indenter in kilograms divided by the volume of the indentation produced in cubic millimeters.

Oertel and Pölguter<sup>(19)</sup> determined the hardness of a series of high-speed steels up to 1100° C. (2010° F.), using the method previously developed by Wüst and Bardenheuer<sup>(24)</sup> in which a mounted ball weighing 2.2 lb. (1 kg.) was dropped from a given height (15.7 in.—400 mm.) on to the specimen and the diameter of the impression measured. From a calibration curve worked out by making tests on materials of different hardnesses their impact-hardness values were converted into Brinell values. Their results gave curves very similar to those obtained in the present investigation. The compositions and the hardness of their steels at room temperature and at 700° C. (1290° F.) are given in Table 2. Their steels 1 and 2 are of the high-tungsten high-vanadium and high-

tungsten low-vanadium types, respectively. By comparing their results at 700° C. (1290° F.) with those given in Tables 9 and 12, it will be seen that they obtained much higher values. Their other steels are not comparable in analysis to any steels included in this study.

TABLE 2.—Impact Hardness of High-speed Steel at 700° C. (Oertel and Pölzguter's Data)

Steel No.	Chemical Composition, Per Cent						Hardness, Brinell	
	C	Cr	W	Mo	Co	V	25° C. 75° F.	700° C. 1290° F.
1	0.70	4.50	20.3	0.5		1.4	670	380
2	0.81	4.76	18.8			0.4	665	360
3	0.83	0.47	13.1			0.4	665	380
4	0.80	5.06		6.37			665	250
5	1.06	4.70		7.27	6.67	1.4	660	200

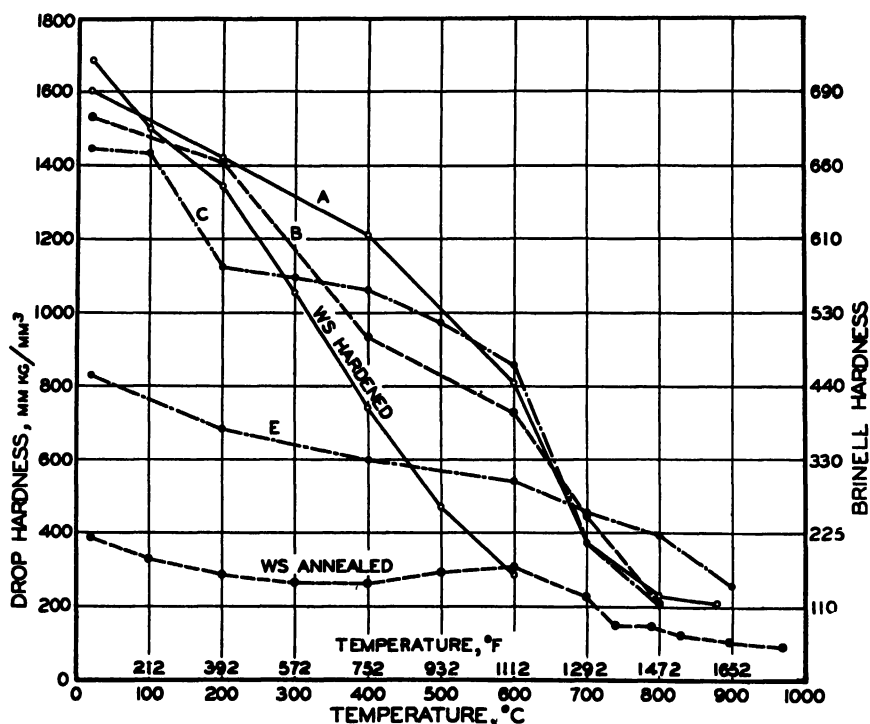


FIG. 1.—IMPACT HARDNESS OF HIGH-SPEED STEELS AT DIFFERENT TEMPERATURES (Körber and Simonsen<sup>17</sup>).

Cutting tests were reported for steels 4 and 5, in which cutting times of 9 and 22 min. respectively were found. It will be noted that the steel

of somewhat lower hardness at 700° C. (1290° F.) showed a much longer cutting time.

The hot-hardness of three high-speed steels and a chromium-cobalt-molybdenum alloy of one of the Stellite types was determined by the "drop-hardness" method by Körber and Simonsen<sup>(17)</sup> for temperatures up to 800° to 900° C. (1470° to 1650° F.). The method used was that previously described by Wüst and Bardenheuer.<sup>(24)</sup> The compositions and the hardness values for tests at room temperature, 600° and 700° C., (1110° and 1290° F.) are given in Table 3, in which the values are in millimeters times kilograms divided by cubic millimeters, as reported by the authors, although the curve worked out by Wüst and Bardenheuer makes it possible to convert the "drop-hardness" values into Brinell numbers, which are given at the right of Fig. 1. Their curves are of the same general character as those found in the present study.

TABLE 3.—*Impact Hardness of High-speed Steels.\* (Körber and Simonsen)*

Steel No.	Chemical Composition, Per Cent							Impact Hardness, Mm Kg /Cu Mm		
	C	Cr	W	V	Co	Mo	Ni	20° C 70° F	600° C 1110° F	700° C 1290° F
A	0 76	5 22	18 8	0 13		0 55		1600	810	375
B	0 74	3 81	11 5	0 19		0 90		1530	730	445
C	0 65	4 21	18 3	0 46	3 89	0 67	0 45	1445	860	375
E (Stellite)	1 20	9 20	(1 52 Mn)		55 9	19 7		830	540	453

\* A quenched from 1200° C (2190° F.), B from 1250° to 1290° C. (2280° to 2350° F.), and C from 1200° C. (2190° F.) and tested as quenched.

A plain-carbon steel (1.06 per cent C) tested as annealed and as hardened is included in the curve marked *WS*, for comparison.

Using a steel analyzing C, 0.60; W, 14.0; Cr, 3.5; V, 0.25 per cent, Page<sup>(20)</sup> determined the hot-hardness by the impact method upon quenched and tempered specimens. The quenched specimens showed a minimum in the hot-hardness curve at 400° C. (750° F.) and a maximum at 550° C. (1020° F.). When the specimens were heated to 1250° C. (2280° F.), held at this temperature 5 min., quenched, and tempered 10 min. at 600° C. (1110° F.), a curve similar to those reported by other investigators was obtained.

In general, it may be said that the character of the hot-hardness curves obtained by the impact method is similar to those obtained by other methods, although exact values may differ and the slopes of the curves may vary somewhat.

*Results of Method C.*—Rapatz and Kallen<sup>(21)</sup> have studied the hot-hardness of six high-speed steels, the compositions of which are given in Table 4.

TABLE 4.—*Chemical Compositions of the Second Experimental Series (Rapatz and Kallen's Data)*

Steel Designation	Composition, Per Cent					
	C	Cr	W	V	Co	Mo
A	0.72	4.60	15.5	1.15	9.0	0.65
B	0.70	4.55	21.0	1.95		0.70
C	0.70	4.00	13.0	2.00		0.07
D	0.70	4.10	18.0	1.30		0.10
E	0.75	4.25	19.5	0.50		
F	0.75	4.00	16.0			0.40

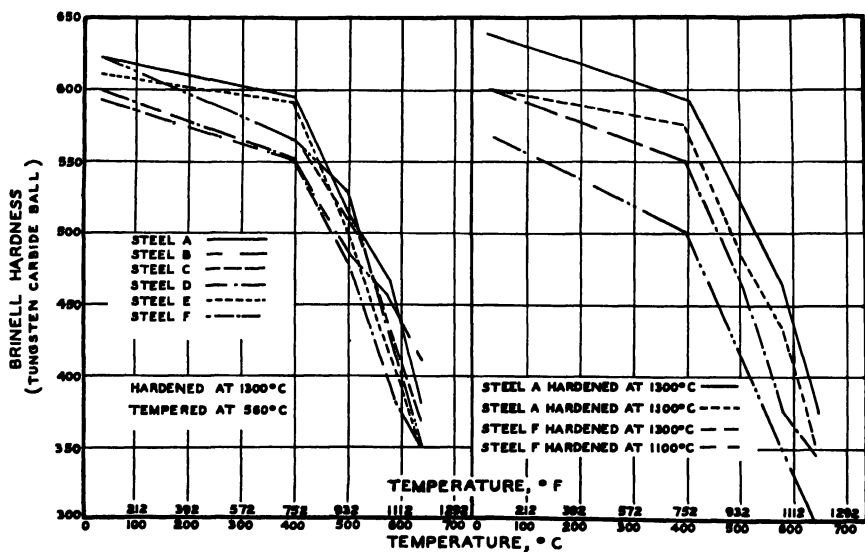


FIG. 2.—BRINELL HARDNESS OF HIGH-SPEED STEELS AT DIFFERENT TEMPERATURES AND EFFECT OF QUENCHING TEMPERATURE ON HARDNESS. (Rapatz and Kallen<sup>21</sup>).

The steels were quenched from 1300° C. (2370° F.) and tempered at 560° C. (1040° F.). The specimens were brought to temperature, held at temperature for about 20 min. and then tested by applying a load of 700 kg. on a tungsten carbide (Widia) hemisphere. About 10 sec. was used in applying the full load, which was maintained for about that same length of time. Hardness determinations were made at 400°, 500°, 580° and 600° C. (750°, 930°, 1075° and 1110° F.). The results of the tests are shown in Fig. 2.

Apparently these investigators multiplied the hardness values obtained by this method by the factor of 1.25, in order to make them comparable with the hardness that would be obtained with the ball of this size and a load of 3000 kg. Steels A and F were also used to study the effect of hardening temperature on the hot-hardness. The results are shown in the same figure, in which the steels were tested in the hardened condition after quenching from 1100° and 1300° C. (2010° and 2370° F.). The results show clearly that increasing the hardening

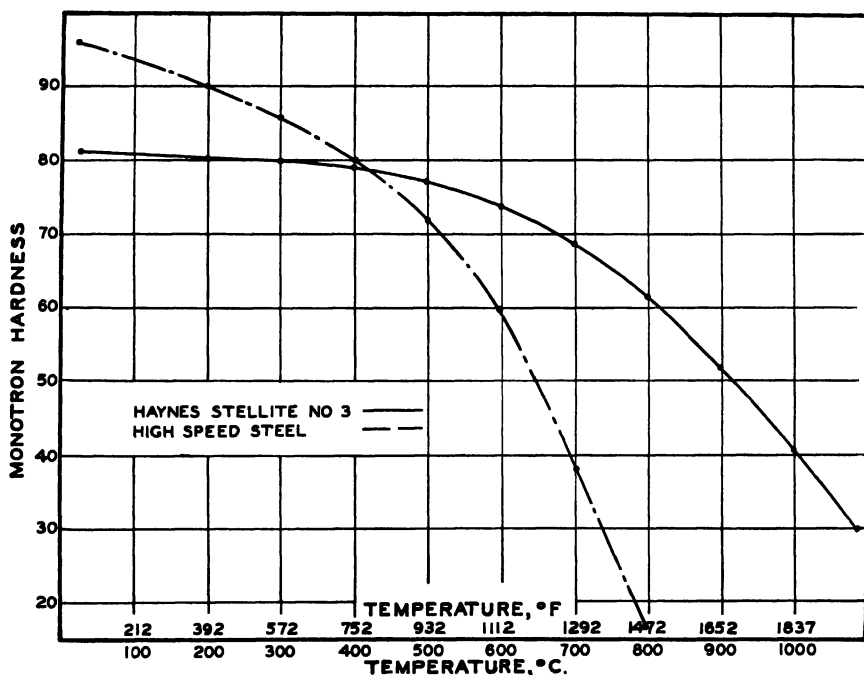


FIG. 3 — MONOTRON HARDNESS OF HIGH-SPEED STEEL AND HAYNES STELLITE NO. 3 AT DIFFERENT TEMPERATURES. (Grossmann and Bain<sup>11</sup>).

temperature over this range increased both the original hardness and the hardness at elevated temperatures of these steels.

The investigation by these authors differs from other Brinell hardness tests at elevated temperatures, in that the indenting ball was at the same temperature as the steel specimens being tested.

The Union Carbide and Carbon Research Laboratory has used the Monotron hardness tester to determine the hardness of various kinds of Stellite and high-speed steels at elevated temperatures.<sup>(12)</sup> In their tests the specimens were held at the testing temperature for 1½ hr., after which the test was made in the usual way of using the Monotron tester, except that the indenter was at the testing temperature. The

results of tests by this method on a high-speed steel and on Haynes Stellite No. 3 (similar to No. 50, Table 5) are shown in Fig. 3 from Grossmann and Bain.<sup>(11)</sup> It will be observed that the curves are of the same general character as those found in this study, except that the hardness of the Stellite becomes greater than that of the high-speed steel at a somewhat lower temperature than was found in the present study. (See Fig. 15.)

Herbert<sup>(13)</sup> has applied the Herbert pendulum to the testing of hot-hardness of high-speed steel, nitrided steel and a 1.25 per cent carbon steel. The results of his tests are shown in Fig. 4. The curves that Herbert

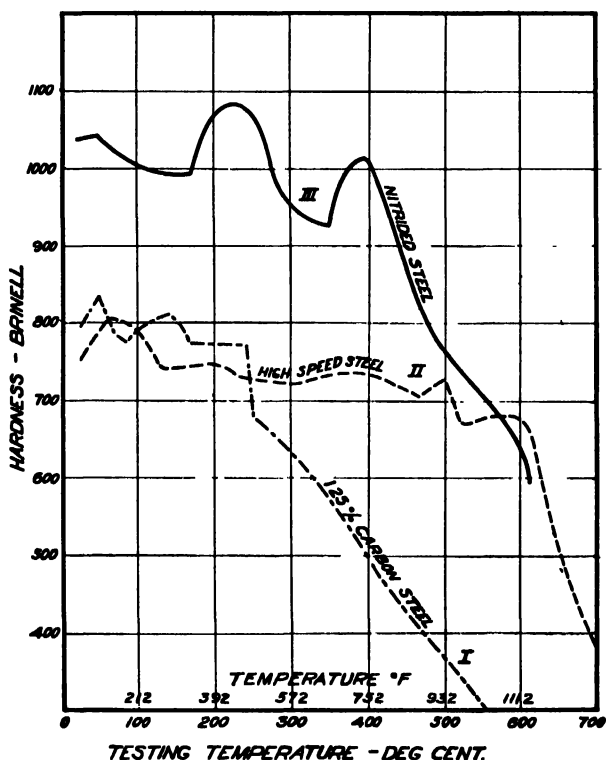


FIG. 4—PENDULUM HARDNESS OF HIGH-SPEED, CARBON, AND NITRIDED STEELS AT DIFFERENT TEMPERATURES. (Herbert<sup>13</sup>).

obtained are much more irregular in shape than those obtained by previous investigators or those found in the present study.

#### *Hot-hardness of Pure Metals*

In considering the hot-hardness of high-speed steels and the component elements that may contribute to hot-hardness, it is of interest to note the hot-hardness of some of these component metals, and this

information may be obtained by reference to Fig. 5, taken from Grossmann and Bain.<sup>(11)</sup> The maximum hardness is shown by tungsten. This is followed by molybdenum, but the elements chromium and cobalt show a lower rate of loss of hardness with increase in temperature than either tungsten or molybdenum.

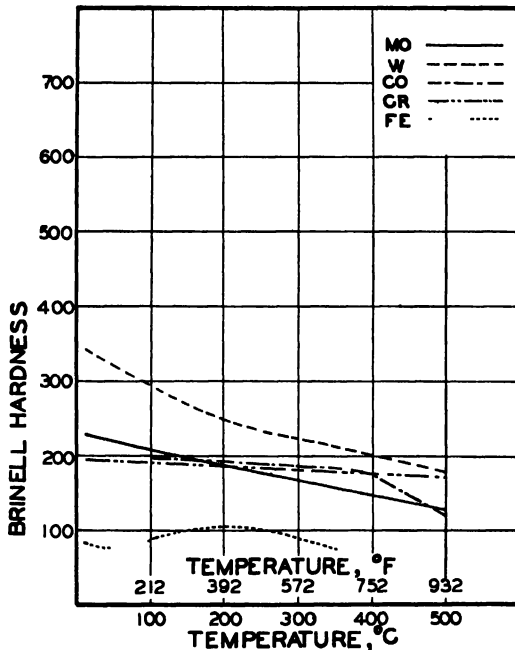


FIG 5.—BRINELL HARDNESS OF TUNGSTEN, MOLYBDENUM, COBALT, CHROMIUM AND IRON AT DIFFERENT TEMPERATURES. (Grossmann and Bain<sup>11</sup>).

### *Temperatures Developed in Metal Cutting*

Herbert<sup>(14)</sup> used the cutting tool and the metal being planed or turned as two elements of a thermocouple, and by this means measured the temperature at the contact. In one test, in which he was using a depth of cut of 0.0012 in. and a feed of  $\frac{1}{16}$  in., he observed that a temperature of 700° C. (1290° F.) was developed at a cutting speed of 200 ft. per minute when the cutting was done dry. Under similar conditions, when the tool was flooded with water a temperature of 500° C. (930° F.) was observed. In a related test on mild steel with a cut of  $\frac{1}{8}$  in. and a feed of 0.003 in. a temperature of 500° C. (930° F.) was observed at a feed of only 60 ft. per minute when the cutting was done dry. In the case of a shaper tool operating at 68 strokes per minute on mild steel he observed a temperature well above 600° C. (1110° F.), the maximum temperature measurable with the equipment at hand, which he estimated to have been above 700° C. (1290° F.).



O. W. Boston<sup>(1)</sup> has advised that, by using a cutting tool of high-speed steel of the 18-4-1 type\* as one element of the thermocouple and the steel being turned as the other, he has measured operating temperatures up to 1200° F. (650° C.). The fact that cutting tools in heavy service have been observed to show a red heat shows that temperatures in the range of 600° to 700° C. (1110° to 1290° F.) may be encountered.

The importance of high-speed tools retaining their hardness at elevated temperatures has been well stated by Grossmann and Bain<sup>(10)</sup> as follows:

. . . Regardless of whether the subsequent *room temperature* hardness is impaired or not by the heat of cutting—the tool must be hard *at the temperature* developed by the desired cutting rate if the tool is to meet a specified demand. It, therefore, becomes evident what the term red-hardness as applied to hardened high-speed steel signifies. A cutting tool possesses red-hardness if at the visibly red heat developed in service it still maintains substantially its cutting hardness.

## PART I.—EXPERIMENTAL STUDY OF THE HOT-HARDNESS OF HIGH-SPEED STEELS AND RELATED ALLOYS

### *Materials Used in the Investigation*

The materials used in the investigation are listed in Table 5, in which the chemical compositions as reported by the manufacturer are given. A survey of this table shows that steel No. 22 is a molybdenum high-speed steel in which 9.50 per cent of molybdenum was used to entirely replace the tungsten. Steels 24, 26, 32, 33 and 41 are representative of the 18 per cent tungsten, 4 per cent chromium and 1 per cent vanadium type. Steels 38 and 42 are representative of the high-vanadium type, in which the vanadium is about 2 per cent. However, No. 38 is of the 14 per cent tungsten type and No. 42 of the 18 per cent tungsten type, and 42 is further modified by the addition of 1.3 per cent of molybdenum. Steel 48 is of the high-carbon high-vanadium type. Steels 23, 25, 28, 29, 30, 31, 37, 39, 40, 43 and 44 are cobalt-containing steels and are representative of the high-tungsten high-vanadium and high-tungsten low-vanadium and low-tungsten high-vanadium types. Nos. 28 and 29 are not high-speed steels but are die steels of the chromium-cobalt type and do not contain tungsten or vanadium.

Other steels which are not typical high-speed steels are No. 34, a die steel; No. 35, a low-carbon steel for hot working; and No. 36, a steel for wood-working tools. Steels 52 and 53 are of the austenitic type recently described by Ehmcke,<sup>(6)</sup> the former containing nickel and the latter manganese as the austenitizing elements. Samples 50 and 51 are of the cobalt-chromium type of material, while 54 is an alloy used largely for hard-coating wearing surfaces.

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\* Approximately 18 per cent W, 4 per cent Cr and 1 per cent V.

Samples of these materials were furnished gratis by the manufacturers, and in general the samples were received in the size of  $\frac{1}{2}$  to  $\frac{5}{8}$ -in. round stock. Specimens were machined to about 0.040-in. oversize and cut into

TABLE 5.—*Chemical Composition of Materials Used*

Steel No.	C	W	Cr	V	Mo	Co	Mn	Ni	Si
22	0.70	---	5.50	1.20	9.50	---	---	---	---
23	0.80	19.00	4.00	2.00	1.00	7.00	---	---	---
24	0.70	18.00	4.00	1.00	---	---	---	---	---
25	0.75	18.00	4.00	1.00	---	8.00	---	---	---
26	0.68	18.00	4.00	1.00	---	---	---	---	---
28	1.50	---	11.00	---	0.75	3.00	0.20	0.40	0.40
			to		to	to	to	to	to
			15.00		0.90	3.50	0.50	0.50	0.60
29	"	"	"	"	"	"	"	"	"
50	0.60	17.00	5.75	1.00	0.50	5.75	0.20	---	0.20
	to	to	to	to	to	to	to	---	to
	0.70	18.00	4.25	1.25	1.00	4.25	0.55	---	0.50
31	"	"	"	"	"	"	"	---	"
32	0.72	18.00	4.00	1.25	---	---	0.25	---	0.25
35	0.78	18.00	4.00	1.25	---	---	0.25	---	0.25
34	2.50	10.50	1.85	---	---	---	1.90	---	0.60
35	0.40	18.50	5.75	0.65	---	---	0.50	---	0.25
36	1.25	8.00	4.00	---	---	---	0.25	---	0.45
37	0.70	14.00	4.00	2.0	---	5.85	0.15	---	0.25
38	0.72	14.25	4.25	2.00	---	---	---	---	---
39	0.70	18.25	4.15	0.90	---	5.20	---	---	---
40	0.70	18.25	4.00	1.25	0.55	6.00	---	---	---
41	0.70	18.25	4.15	0.90	---	---	---	---	---
42	0.75	18.36	4.14	1.99	1.80	---	0.25	---	0.55
43	0.74	17.05	4.15	1.04	0.50	4.55	0.58	---	0.27
44	0.74	18.18	5.99	1.91	0.64	6.69	0.55	---	0.26
45	0.70	18.25	4.50	2.00	---	15.00	0.40	---	0.30
46	0.45	18.0	5.50	---	---	---	0.30	---	0.50
47	0.75	18.56	4.19	---	---	---	---	---	---
48	1.40	18.69	4.07	5.52	---	---	---	---	---
49	0.79	21.70	4.34	1.40	0.41	11.74	---	---	---
50 <sup>a</sup>	2.00	12.0	30.0	---	---	44.0	---	---	---
	to	to	to	---	---	---	---	---	---
	3.00	14.0	35.0	---	---	46.0	---	---	---
51 <sup>a</sup>	2.00	14.0	32.0	---	---	44.0	---	---	---
	to	to	to	---	---	---	---	---	---
	3.00	17.0	34.0	---	---	46.0	---	---	---
52	0.75	17.81	5.86	0.76	1.24	---	0.54	7.57	0.41
53	0.81	18.54	5.70	0.81	1.10	---	4.28	---	0.55
54 <sup>b</sup>	5.00	25.00	15.00	1.00	---	---	---	5.00	1.00

<sup>a</sup> These alloys contain some iron, silicon, manganese, etc

<sup>b</sup> Balance of this alloy, iron

6-in. lengths, after which they were heat-treated as indicated in Table 6, then ground to a diameter of 1 cm. and cut to exact length. Materials 50, 51 and 54 were tested in the as-cast condition, and the samples were prepared by the manufacturers.

### Heat Treatments

The heat treatments used are shown in detail in Table 6. In general these heat treatments followed closely the recommendations of the manufacturer. The original plan was to bring all materials to the hardening temperature and hold 5 min. at that temperature, then quench in oil at a temperature of about 100° F., (40° C.) and reheat 2 hr. at the selected

tempering temperature. In the case of some of the high hardening temperatures, some difficulty was experienced in holding the samples 5 min. at temperature, and, as indicated in the table, some of them were held only 2 min. at temperature. Treatments other than those following this general scheme were those recommended by the manufacturer. Steels 28 and 29 represent the same analysis, but the heat treatment used on 28 is the one recommended by the manufacturer while the one used on 29 was selected as more in keeping with the heat treatment of high-speed steels, and significant results were obtained, as will be indicated later.

TABLE 6.—Heat Treatment

Steel No.	Preheating Temperature		Hardening			Quenching Medium <sup>b</sup>	Tempering		
	°F.	°C.	°F.	°C.	Time, Min. <sup>a</sup>		°F.	°C.	Time
22 <sup>c</sup>	1550	845	2150	1180	5	Oil	950	500	2 hr.
23	1625	885	2400	1315	2	Oil	1100	595	2 "
24	1625	885	2350	1290	5	Oil	1075	580	2 "
25 <sup>d</sup>	1500	815	2400	1315	2	Oil	1050	565	2 "
26	1550	845	2350	1290	5	Oil	1050	565	2 "
28	1500	705	1850	1010	5	Still Air	1150	620	10 min.
29	1800	705	2100	1150	5	Oil	1000	540	2 hr.
30	1500	815	2400	1315	2	Oil	1150	620	2 "
31	1500	815	2400	1315	2	Still Air	1150	620	2 "
32	1500	815	2350	1290	5	Oil	1075	580	2 "
33	1500	815	2350	1290	5	Oil	1075	580	2 "
34	1800	705	2100	1150	5	Oil	1000	540	2 "
35	1500	815	2350	1290	10	Oil	1050	565	2 "
36	1300	705	2000	1090	5	Oil	1050	565	2 "
37	1500	815	2350	1290	5	Oil	1075	580	2 "
38	1675	865	2500	1280	5	Oil	1100	595	2 "
39	1675	865	2500	1280	5	Oil	1100	595	2 "
40	1675	865	2400	1315	2	Still Air <sup>d</sup>	1075	580	2 "
41	1675	865	2500	1280	5	Oil	1100	595	2 "
42	1550	845	2350	1290	5	Oil	1050	565	2 "
43	1600	870	2550	1290	5	Oil	1050	565	2 "
44	1600	870	2550	1290	5	Oil	1050	565	2 "
45	1500	815	2550	1290	5	Air Blast <sup>f</sup>	1175	635	2 min.
46	1500	815	2500	1280	5	Still Air	1150	620	2 hr.
47	1800	870	2550	1290	5	Oil	1075	580	2 "
48	1500	815	2350	1290	5	Oil	1050	565	2 "
49	1500	815	2400	1315	1-2	Oil	1050	565	2 "
50	Used in the cast condition								
51	"	"	"	"	"				
52	1500	815	2280	1250	5	Oil	1470	800	2 "
53	1500	815	2280	1250	5	Oil	1470	800	2 "
54	Used in the cast condition								

<sup>a</sup> Time after specimen came to temperature

<sup>b</sup> The quenching oil was kept at about 100° F. (40° C)

<sup>c</sup> Protected with borax.

<sup>d</sup> Placed in drawing furnace when cooled to 400° to 600° F. (200° to 320° C).

<sup>e</sup> Heated first to 1100° F. (590° C.) and then to 1800° F. (870° C).

<sup>f</sup> Cooled to black heat and then quenched in oil

The effects of using an air quench, as compared with an oil quench, will be discussed under "Results."

### Microscopic Examination

Microscopic examination was made on all samples of steels in the as-received condition, as quenched and as tempered. Macro-etches were

also made on the materials in the as-received condition, which showed all samples to be sound and satisfactorily homogeneous, as is shown in Fig. 6. The micro and macro examinations of the materials as received served to indicate that they had been previously processed in such a way as to produce satisfactory structures, while the examination of the heat-treated specimens served to show that normal structures had been obtained both with regard to grain size and size and distribution of carbide particles, and the examination of the specimens after tempering gave some information with reference to the changes in structure. Only two structures were sufficiently different from those expected to require mentioning here.

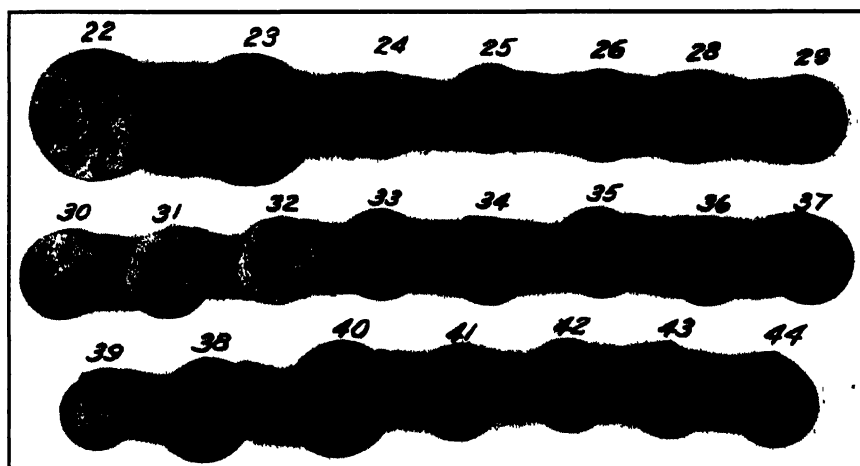


FIG 6 — MACROSTRUCTURES OF STEELS AS RECEIVED. ETCHED 45 MINUTES IN HOT 1:1 HYDROCHLORIC ACID. APPROXIMATELY EXACT SIZE.

Steel 35, which was held 10 min. at the hardening temperature of 2350° F. (1290° C.), seemed to show evidence of overheating, as may be seen in Fig. 7. The same may be said of steel 30, which was held 5 min. at the hardening temperature of 2400° F. (1320° C.). Fig. 8 shows that some of the carbides have sharp corners, which is generally associated with high quenching temperatures. In no case, however, was any eutectic noted, and the grains were not excessively coarsened.

#### *Testing Method and Equipment*

The mutual-indentation method of determining the hardness of metals as developed by Cowdrey<sup>(3)</sup> was used in this study. Cowdrey conducted his tests by using cylinders in parallel position. He experimented with different sizes of cylinders, both in regard to length and diameter, and from his investigation it appeared that cylinders 1 cm. in diameter and 1 cm. long were well suited for the determination of the hardness of mate-

rials within the range expected in the high-speed steels for temperatures up to 800° C. (1470° F.). This choice proved satisfactory. For most of the materials a load of 1000 kg. had to be used at 700° C. (1290° F.) and a load of 500 kg. at 800° C. (1470° F.). For the lower temperatures a load of 3000 kg. was used.

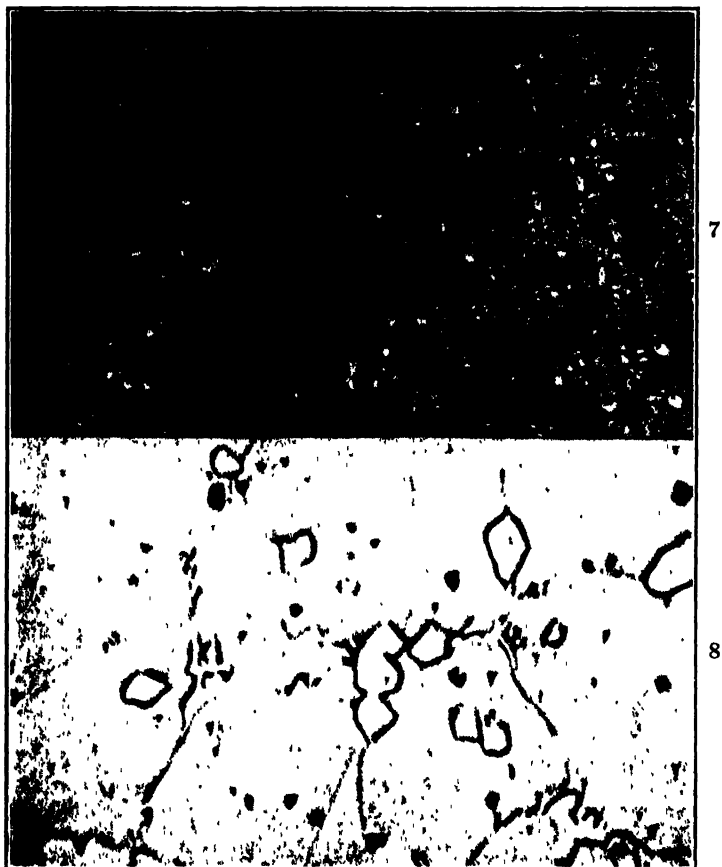


FIG. 7.—MICROSTRUCTURE OF STEEL NO. 35, QUENCHED FROM 2350° F. (1290° C.) ETCHED IN 2 PER CENT NITAL.  $\times 1000$ . THE DARK AREAS MAY BE DELTA IRON.

FIG. 8.—MICROSTRUCTURE OF STEEL NO. 30 QUENCHED FROM 2400° F. (1315° C.). ETCHED IN 2 PER CENT NITAL.  $\times 1000$ . NOTE ANGULAR CARBIDES.

In making the tests, two cylinders 1 cm. long and 1 cm. in diameter were placed in parallel position and the desired load applied for 30 sec. The width of the flattened or indented surface was then measured at a magnification of about 10 (using a Brinell microscope), and this reading in millimeters times the length (10 mm.) gave the area of the indented surface. The cylinder hardness is then calculated from the equation:

$$\text{Cylinder Hardness} = \frac{\text{Applied Load in Kilograms}}{\text{Area of Indentation in Square Millimeters}}$$

Cowdrey<sup>(3)</sup> found that he obtained a satisfactory relation between the usual Brinell hardness and the hardness determined by the use of cylinders if he used the following equation:

$$\text{Brinell Hardness} = 1.52 \times \text{Cylinder Hardness Number}$$

and this conversion factor has been used throughout the present study. Cowdrey's recommendation with reference to determining the area of the

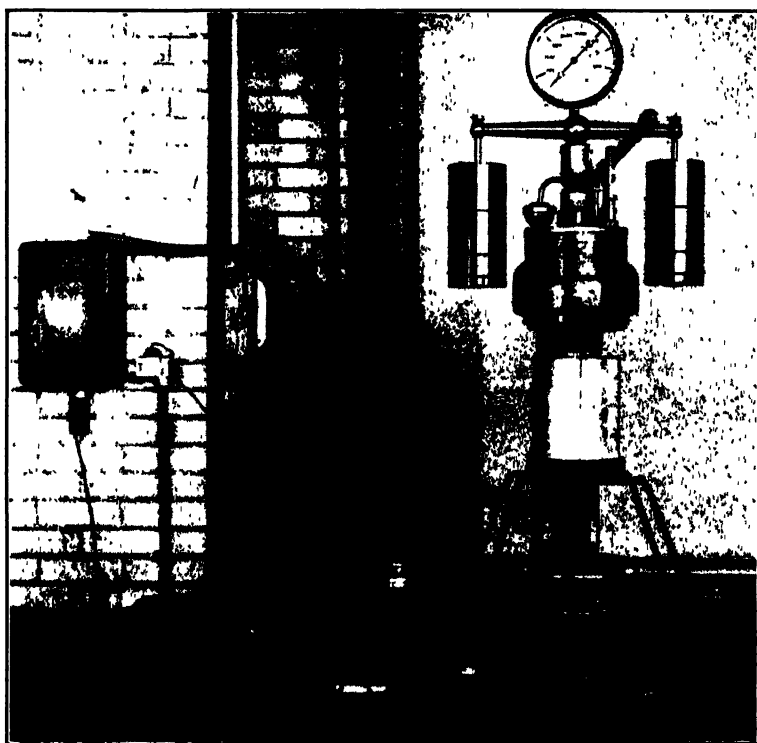


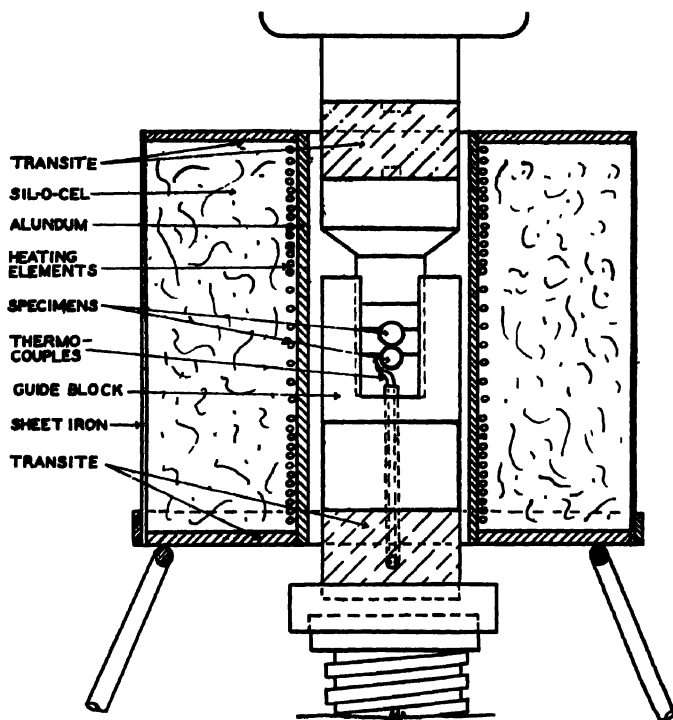
FIG. 9.—TESTING ASSEMBLY.

flattened surface has been followed—that is, the maximum width times the original length of the cylinder gives the area of the flattened surface. The data in Table 8, which show the hardnesses at 200° and 300° C. (390° and 570° F.) as determined by the mutual indentation method and by the standard Brinell method using a tungsten carbide ball, show that the reliability of Cowdrey's equation has been confirmed within the range of experimental accuracy.

The apparatus employed in the present study consisted, in general, of a hydraulic type Brinell hardness testing machine, a small gap-wound

electric furnace, and a set of compression blocks for holding the cylinders in place during the test. A photograph of a typical set-up is shown in Fig. 9, and the drawing shown in Fig. 10 gives some details of the testing assembly.

The compression blocks were made of a chromium-nickel steel of the following composition: C, 0.40; Si, 1.30; Ni, 18.0; Cr, 25.0 per cent. These blocks were made in one piece and the hole drilled and reamed to



TESTING ASSEMBLY

FIG. 10.—FURNACE AND COMPRESSION BLOCKS WITH THERMOCOUPLE.

size, after which the block was cut in two with a narrow milling saw, to form the two compression blocks.

These two compression blocks fitted in the slot of a guide block, which was made of the same material. This guide block was used for supporting and keeping the two compression blocks in place. It also centered and lined up the assembly with the ram and anvil of the Brinell machine. (See Fig. 9.)

Part of the upper ram and a section of the base were made of "transite," to prevent heat loss as much as possible.

The temperature of the specimens was controlled by means of a chromel-alumel couple of No. 22 gage wire inserted in the base of the compression block as shown in Fig. 10. This couple was then connected to a Wilson-Maeulin automatic controller and also to a potentiometer for reading the temperature. The current through the furnace could be varied by means of two resistance coils and a carbon rheostat connected in series with the heating circuit.

TABLE 7.—*Room-temperature Hardness as Determined by Different Methods*

Steel No.	Brinell <sup>a</sup>		Rockwell C <sup>b</sup>		Vickers-Brinell <sup>b</sup>	
	Quenched	Tempered	Quenched	Tempered	Quenched	Tempered
22	780	682	64.6	65.5	872	828
25	627	694	62.7	65.5	714	817
24	---	694	64.0	65.6	---	758
25	712	712	65.7	65.7	774	808
26	---	688	65.4	62.6	---	704
28	745	415	65.5	44.5	805	416
29	415	601	51.5	59.6	528	722
30	708	665	65.7	65.8	825	885
31	694	645	64.8	61.8	762	866
32	712	724	64.7	64.7	807	850
33	780	655	66.1	65.2	922	752
34	282	627	55.0	61.9	280	720
35	578	527	57.0	55.5	702	576
36	289	514	58.5	55.2	288	552
37	745	688	65.6	64.5	852	756
38	712	655	65.6	61.5	860	707
39	719	712	64.7	65.0	795	822
40	---	700	---	64.5	---	784
41	725	700	65.1	64.0	800	725
42	712	645	65.4	61.4	845	687
43	700	745	65.6	65.6	850	915
44	712	712	64.5	64.8	840	852
45	655	694	62.0	64.0	751	852
46	627	514	60.5	55.7	700	544
47	712	655	64.0	61.2	852	694
48	---	700	66.5	65.6	---	928
49	655	712	65.6	64.5	754	694
52	289	578	52.0	56.6	322	590
55	321	627	40.4	61.0	345	680
Hardness As Received						
50			58.2	755		
51			60.1	775		
54			54.8	612		

<sup>a</sup> Tungsten carbide ball used.

<sup>b</sup> Average of five tests.

In making a test the furnace and the compression units were first heated to the desired testing temperature. The compression assembly was then lowered, the two cylinders to be tested were inserted, and the unit again raised to the position shown in Fig. 10.

It required some 5 to 10 min. to heat the specimens to temperature, depending upon the particular testing temperature. In all cases the specimens were held at the testing temperature for 20 min., and the load was applied for 30 sec. This procedure was adopted after tests had been made with a thermocouple in one of the cylinders, and a curve had been



drawn to show the relation between the temperature of the compression block and the cylinder under tests.

The temperatures reported are accurate to within less than 1 per cent in the red-heat range. Further refinement in temperature control could

TABLE 8.—*Mutual-indentation Hardness at 200° and 300° C. (390° and 570° F.) Compared with Brinell Hardness Obtained with a Tungsten Carbide Ball*

(Quenched and Tempered Specimens)

B.M.I. No.	Mutual Indentation Brinell Hardness	Brinell Hardness	Per Cent Difference
<u>Tests at 200° C. (390° F.)</u>			
22	640	655	-1.5
25	670	655	+2.6
24	681	682	---
25	672	655	+2.9
26	675	655	+5.9
28	586	571	+2.6
29	550	555	-4.5
30	645	655	-1.5
31	654	627	+1.1
32	724	712	+1.6
35	654	645	+1.4
35	490	477	+2.7
36	460	452	+1.7
38	608	611	-0.5
39	701	697	+0.6
40	661	655	+1.2
41	697	672	+1.7
42	645	645	---
43	702	700	-0.6
45	646	648	-0.3
46	506	477	+6.0
47	654	645	-1.4
48	701	694	+1.0
49	672	655	+2.9
<u>Tests at 300° C. (570° F.)</u>			
22	608	601	+1.1
25	654	655	---
24	658	648	+1.5
25	652	645	+1.4
26	650	655	-0.5
28	365	355	+2.8
29	517	540	+4.2
30	625	657	-1.9
31	616	601	+2.4
32	708	698	+1.9
35	624	632	-1.5
35	456	444	+2.7
36	459	442	-0.7
38	570	589	-5.2
39	650	659	-1.5
40	625	645	-5.1
41	650	621	+2.8
42	635	601	+5.1
43	671	682	-1.6
45	654	645	+1.7
46	456	444	+2.7
47	616	627	-1.7
48	672	655	+2.9
49	661	645	+2.6

be obtained, but obviously need not be sought unless and until some valuable correlation of hot-hardness values and tool performance is tentatively established. The minimum time per test using the present procedure is about 30 minutes.

*Discussion of Results*

The results of the hardness tests at room temperatures by different methods are shown in Table 7. It will be observed from the Rockwell C hardness values that normal hardnesses have been obtained in both the quenched and tempered conditions.

The hardness by the mutual-indentation method and by the standard Brinell method, using a tungsten carbide ball for tests at 200° and 300° C.

TABLE 9.—*Hot-hardness Tests on Tempered Specimens by the Mutual-indentation Method*

B. M. I. No.	200°C. 390°F.	300° C. 570° F.	400°C. 750°F.	500°C. 950°F.	600°C. 1110°F.	700°C. <sup>a</sup> 1290°F.	800°C. <sup>b</sup> 1470°F.
22	640	610	590	565	465	150	70
25	670	655	625	570	500	295	65
24	680	660	655	565	480	160	50
25	670	650	625	590	510	505	60
26	675	650	640	560	455	170	50
28	565	565	555	290	170	95	60
29	550	515	470	425	215	55	60
30	645	625	615	585	480	255	60
31	635	615	600	570	470	180	45
32	725	710	640	565	470	220	50
32 <sup>c</sup>	670	585	540	540	480	215	45
35	655	625	590	555	445	215	50
34	610	570	500	435	240	55	65
35	490	455	435	410	350	170	45
36	480	440	400	320	195	70	55
37	670	650	620	575	525	255	65
38	610	570	555	500	435	250	70
39	700	650	625	570	470	240	65
40	640	625	590	570	475	160	50
41	680	650	620	555	440	145	50
42	645	605	570	540	445	280	60
43	700	670	640	600	510	305	65
44	700	645	630	610	510	300	75
45	650	640	625	560	530	255	55
46	505	455	435	380	295	140	45
47	655	615	570	495	350	100	45
48	700	670	655	575	550	505	165
49	670	650	645	610	555	505	75
50	555	520	490	475	475	445	370
51	570	550	505	500	480	455	415
52	505	455	415	385	240	190	135
53	560	505	455	415	235	75	105
54	505	505	445	405	365	275	200

<sup>a</sup> A load of 1000 was employed on all steels at this temperature with the exception of material Nos 50, 51 and 54, on which a 3000-kg load was used

<sup>b</sup> A load of 500 kg. was employed on all steels at this temperature with the exception of material Nos 50, 51 and 54, on which a 3000-kg. load was used.

<sup>c</sup> Hardness tests on "as-quenched" specimens

(390° and 570° F.) is shown in Table 8. This table also shows the percentage difference in the hardness values, and it will be observed that generally there is a fairly good correlation, and the results are both plus and minus, indicating that the differences are largely a matter of experimental error.

The results of the hardness tests by the mutual-indentation method over the temperature range of 200° to 800° C. (390° to 1470° F.) are shown in Table 9, in which the values have been rounded off to the nearest 5. It will be noted from this table that the hardness values of the high-speed

steels have not fallen off to any great extent up to a temperature of 600° C. (1110° F.); also, that on a percentage basis there is no marked difference in the hardnesses of the different steels. When the tests were made at 700° C. (1290° F.), however, a considerable loss in hardness was noted, and there were also marked differences in hardnesses of different materials. From this work it appears that 700° C. (1290° F.) is a critical temperature for determining the hot-hardness, and the results obtained at that temperature will be discussed in considerable detail.

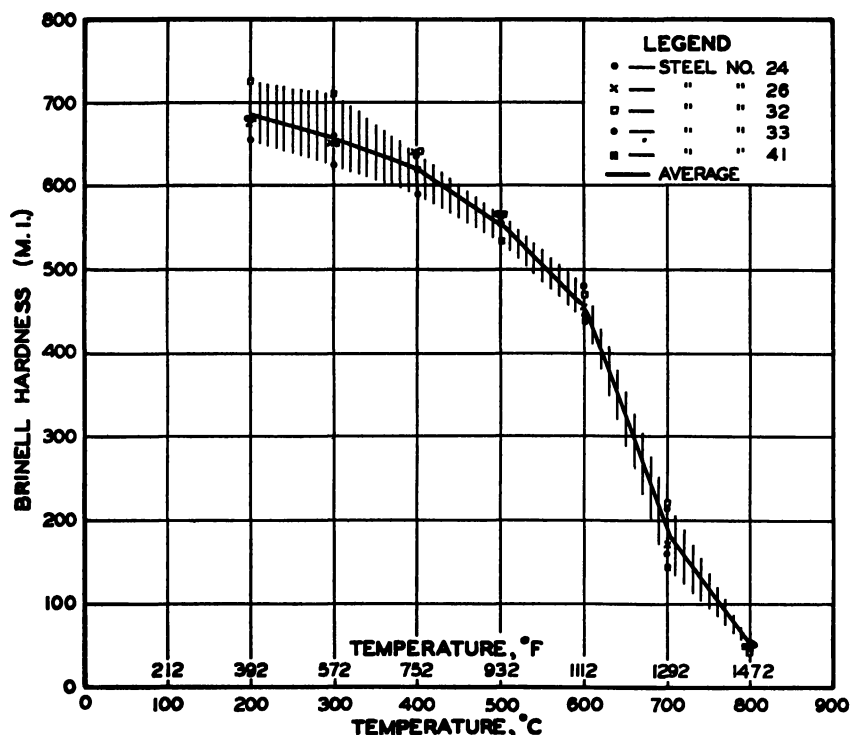


FIG. 11.—HOT-HARDNESS OF 18-4-1 HIGH-SPEED STEELS BY MUTUAL-INDENTATION METHOD.

In passing, it should be mentioned that at 800° C. (1470° F.) practically all of the high-speed steels are soft, the hardness falling to 75 Brinell or under. On the other hand, the nonferrous specimens of the chromium-cobalt type maintained comparatively high hardnesses. From this work it is believed that 800° C. (1470° F.) is too high for significant results in the hot-hardness tests of commercial high-speed steels.

#### *Hot-hardness of 18-4-1 Steels*

Five steels of this type have been examined (Nos. 24, 26, 32, 33 and 41 in Table 5). Individual values for these five steels and a mean average

curve are shown in Fig. 11. The average hot-hardness at 700° C. (1290° F.) for these steels is 182. Steels 32 and 33 show values of 220 and 215 respectively, but Table 5 shows that these two steels contain more than the normal amount of vanadium; that is, 1.25 per cent.

It is of interest to note that steel 39 was reported by the manufacturer to be of the 18-4-1 type, but from the examination of the hardness values at 700° C. (1290° F.) it was noted that this steel showed a hardness of 240. It was suspected, therefore, that it contained some other element which

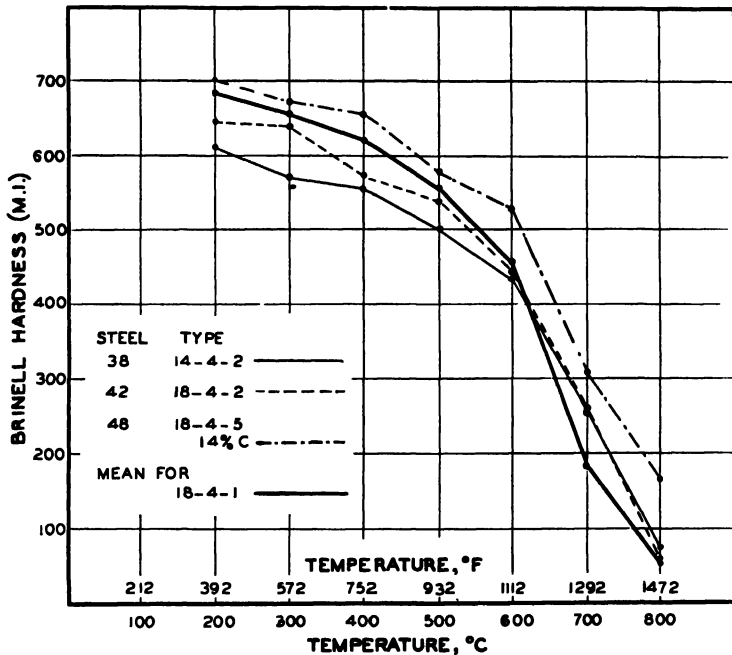


FIG. 12 —HOT-HARDNESS OF HIGH-VANADIUM STEELS COMPARED WITH MEAN FOR 18-4-1 STEELS. TESTS BY MUTUAL-INDENTATION METHOD.

increased the hot-hardness. A chemical analysis was made, and 5.2 per cent of cobalt was found, which places it in the list of cobalt-containing steels with a normal hardness for that type.

### *Effect of Vanadium*

The effect of vanadium on the hardness of high-speed steels at 700° C. (1290° F.) is shown by the data in Table 9 and by the curves in Fig 12. Steels 38 and 42 are of the 2 per cent vanadium type, the former being low-tungsten and the latter being high-tungsten. No. 42 also contains 1.3 per cent of molybdenum. These steels show hot-hardnesses of 250 and 260 respectively, which definitely place them in the class of steels of higher hot-hardness than the 18-4-1 type.

Steel 48 deserves special mention, since it is of the high-carbon high-vanadium (5 per cent vanadium) type, recently described by Kinzel and Burgess,<sup>(16)</sup> and it has a hardness of 305 at 700° C. (1290° F.), again definitely indicating the value of vanadium in inducing hot-hardness. This steel also shows a hardness of 165 at 800° C. (1470° F.), which is considerably higher than any of the other high-speed steels and is more than three times the average hardness of the 18-4-1 type of steels at this temperature.

The efficiency of vanadium in contributing hot-hardness properties to high-speed steels is further indicated by steels 46 and 47, which may be considered as 18-4 steels, differing from the 18-4-1 type only in that they do not contain vanadium. At 700° C. (1290° F.) the average hardness of these two steels is only 120, which is considerably lower than for the normal 18-4-1 high-speed steel.

### *Effect of Cobalt*

The cobalt-containing high-speed steels include Nos. 23, 25, 30, 31, 37, 39, 40, 43, 44, 45 and 49. Steels 28 and 29 are of the chromium-cobalt type of die steel with high carbon but do not contain tungsten. The results of the hardness tests on these cobalt-containing steels at different temperatures are given in Table 9 and are shown by the curves in Figs. 13 and 14. A survey of the results obtained on these steels shows that when they were oil-quenched and tempered in the usual way hardness values at 700° C. (1290° F.) of 250 to over 300 were obtained. Special mention must be made of steel 31, which had the same analysis as No. 30 but was air-quenched, following the manufacturer's recommendation. Air quenching, as compared with oil quenching, gave a hardness value of 180 as against 255 for the oil quench, definitely indicating that better hot-hardness properties are obtained by the oil quench.

Similar comments may be made on steel 40, which, again following the manufacturer's recommendations, was air-quenched. Comparison of the analysis of No. 40 with that of No. 43 shows that they are essentially the same, with the higher tungsten and slightly higher vanadium being found in No. 40, which should favor higher hot-hardness. However, this sample showed only 160 Brinell at 700° C. (1290° F.) while No. 43 showed a hardness of 305, again definitely indicating the advantage of the oil-quenching treatment.

The results that have been obtained on these cobalt-containing high-speed steels show that the addition of cobalt to high-speed steels of the 18-4-1, 18-4-2, or 14-4-2 types further improves the hardness at 700° C. (1290° F.). From the data available it appears that the addition of 4 or 5 per cent of cobalt produces the major effect of increasing the hardness at 700° C. (1290° F.) and that further increase in cobalt has little if any

effect toward raising it. For example, steel 43, with 4.55 per cent cobalt, shows just as high hot-hardness as steel 25, with 8 per cent cobalt, or steel 49, with 11.7 per cent cobalt, and a higher value than steel 45, with

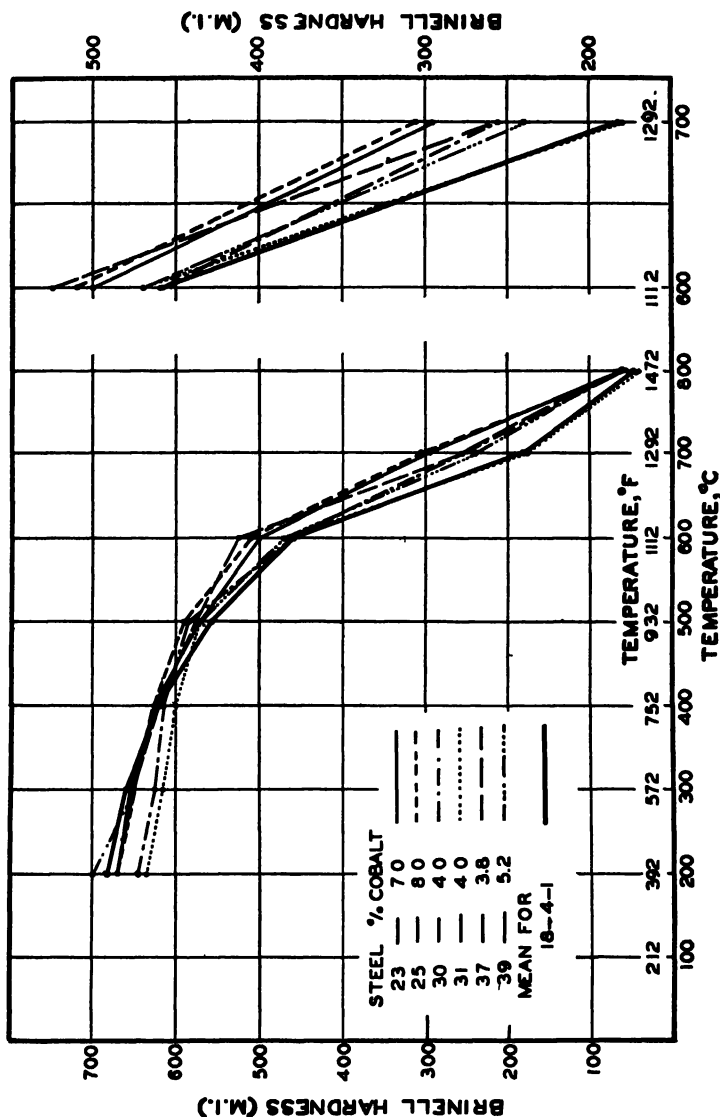


Fig. 13.—HOT-HARDNESS OF COBALT-CONTAINING HIGH-SPEED STEELS COMPARED WITH MEAN FOR 18-4-1 STEELS. TESTS BY MUTUAL-INDENTATION METHOD. FOR OTHER STEELS SEE FIG. 14.

15 per cent cobalt. To be sure, the cobalt may be advantageous in other ways and thus justify its use in larger amounts.

Steels 28 and 29, which are of the same composition but which were subjected to different heat treatments, show that a steel of this composi-

tion (1.5 C, 12 Cr, 3 Co) does not have high hot-hardness. The values were below 100 at 700° C. (1290° F.). This indicates that tungsten, or possibly both tungsten and vanadium, are necessary to give good hot-hardness values.

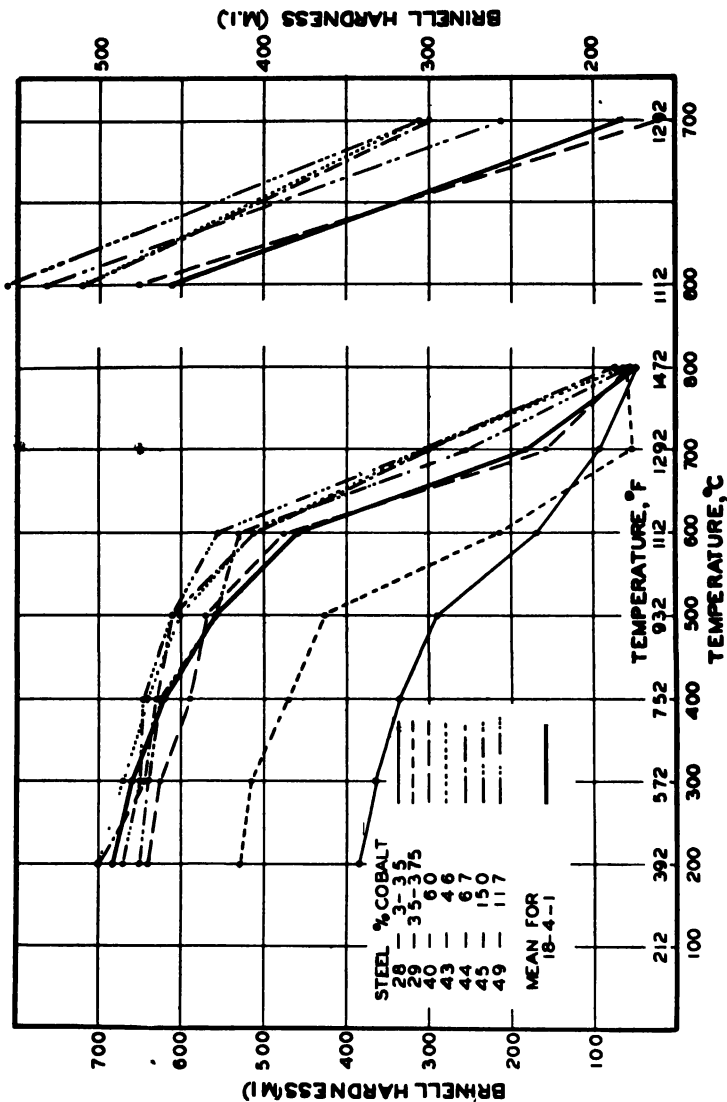


Fig. 14.—HOT-HARDNESS OF COBALT-CONTAINING HIGH-SPEED STEELS COMPARED WITH MEAN FOR 18-4-1 STEELS. TESTS BY MUTUAL-INDENTATION METHOD. FOR OTHER STEELS SEE FIG. 13.

A number of these steels contained a small addition of molybdenum (0.5 to 1 per cent), but no definite conclusions can be drawn from the data with regard to the effects of this element.

### *Hot-hardness of Molybdenum Steels*

Steel 22 is a molybdenum steel in which 9.50 per cent of molybdenum was used instead of all the tungsten. A hardness value of 150 was obtained at 700° C. (1290° F.), which is lower than the average value for the 18-4-1 type of steel. In the tests on the high-speed tools to be discussed later, steel E-29 was also of the molybdenum type (7.07 per cent molybdenum), and showed hardness values at 700° C. (1290° F.) of 150, 180 and 170 for quenching temperatures of 2200°, 2300°, and 2400° F. (1205° to 1315° C.) respectively. These results seem to indicate that the two types of molybdenum steel have lower hardness at elevated temperature than the corresponding types of tungsten-containing high-speed steels.

### *Hot-hardness of Austenitic Steels*

Steels 52 and 53 are the austenitic type and showed a hardness of 190 and 175 respectively at 700° C. (1290° F.). The higher hardness for the nickel-containing steel 52 suggests that nickel is more effective than manganese in contributing hot-hardness properties. These steels showed relatively high hardness values at 800° C. (1470° F.), but it must be remembered that these steels were tempered at this temperature in order to develop the maximum hardness on reheating after quenching.

### *Hot-hardness of Quenched Steels*

Steel 32 was tested in the as-quenched condition and was found to show lower hardness values in the range of 200° to 400° C. (390° to 750° F.) than the tempered specimen of the same steel but the values at 600° C. (1110° F.) and above were practically identical. The values (see Table 9) found for steel 32 in the quenched condition are in good agreement with results previously reported by Page,<sup>(20)</sup> who used an impact hardness test.

### *Miscellaneous Steels*

Steel 34—a die steel containing C, 2.3; W, 10.5; Cr, 1.85; and Mn, 1.9 per cent—had lost considerable hardness even at 600° C. (1110° F.), and at 700° C. (1290° F.) it was only 55 Brinell, which for a steel of this analysis is not comparable even with the 18-4-1 type of high-speed steel on the basis of hot-hardness. Steel 35, which is a low-carbon (0.40 per cent) hot-working steel, corresponding roughly to a 16-4-1 type, showed hot-hardness values only slightly lower than the averages for the 18-4-1 type.

Steel 36, which contained C, 1.25, W, 8.0 and Cr, 4.0 per cent and is recommended for wood-working tools, showed about the same type of hot-hardness as steel 34. Data for these steels are given in Table 9.



*Other Materials*

Only three samples, Nos. 50, 51 and 54, have not been discussed. Nos. 50 and 51 are not steels, but are used for high-speed tools, while No. 54 is used in producing hard surfaces on steel and other metals. The results of the tests on these materials in the cast condition are given in Table 9 and in Fig. 15. The point of special interest regarding Nos. 50 and 51 is that they are lower in hardness than high-speed steels up to

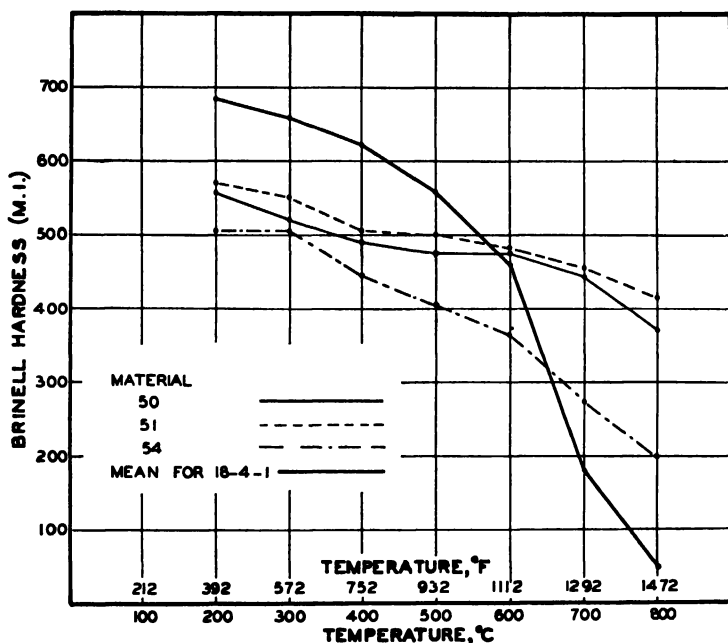


FIG. 15.—HOT-HARDNESS OF SPECIMENS 50, 51 AND 54 COMPARED WITH MEAN FOR 18-4-1 STEELS. TESTS BY MUTUAL-INDENTATION METHOD.

between 500° and 600° C. (930° and 1110° F.) but are much higher at 700° C. (1290° F.) and especially at 800° C. (1470° F.). The same general tendency is shown by No. 54, although the hardness at the higher temperatures is considerably lower.

*Hot-hardness at 650° C. (1200° F.)*

Because of the fact that in considering results in the second part of this investigation in which a fair correlation was found between the hardness of high-speed steel tools at 700° C. (1290° F.) and their Taylor speeds and cutting times, it seemed that the previously observed differences in hot-hardness at 700° C. might be indicative of cutting efficiencies. This conclusion has one rather serious objection in that the hardnesses

observed at this temperature were in many cases so low that it is hardly to be expected that the tools would actually function—the hardnesses observed being actually lower than the hardness of many materials to be machined. It appeared, therefore, that further consideration should be given to a test at 650° C. (1200° F.).

Six specimens were selected to represent three types of steel and the tests made in the usual way. Results are shown in Table 10. There was a considerable loss in hardness in changing from a testing temperature of 600° to 650° C. (1110° to 1200° F.) and the different types of steels showed different orders of hardnesses, as they did at 700° C. For example, the average hardness for the 18-4-1 type was 310, for the 2 per cent vanadium type it was 340, and for the cobalt type about 390. Since these hardnesses are more nearly of the order of magnitude of some of the harder materials to be machined, this testing temperature might prove satisfactory in predicting the cutting efficiency of high-speed tools.

TABLE 10.—*Hot-hardness of High-speed Steels at 650° C. (1200° F.)*

Steel No.	Type of Steel	Hot-hardness by Mutual Indentation		
		600° C. 1110° F.	650° C. 1200° F.	700° C. 1290° F.
24	18-4-1	480	320	160
32	18-4-1	470	304	220
38	14-4-2	435	338	250
42	18-4-2	445	346	260
43	4 55% Co	510	405	305
44	6 69% Co	510	380	300

### *Summary and Conclusion of Part I*

The data thus far reported seem to justify the following tentative conclusions:

1. The mutual-indentation method of hardness testing using cylinders 1 cm. in diameter and 1 cm. long seems well adapted to determine the hardness of high-speed steel and related materials at elevated temperatures.

2. There is a difference in the hardness of high-speed steels when tested at 700° C. (1290° F.), which seems to depend upon composition and heat treatment. It appears that 700° C. (1290° F.) may be a critical temperature for hardness testing as a possible means of predicting cutting efficiencies of high-speed steels, although further tests may show that 650° C. (1200° F.) is a more satisfactory testing temperature.

3. (a) Vanadium is effective in contributing hot-hardness to high-speed steels. The 18-4-1 type, being superior to a similar steel without vanadium and increasing the vanadium to 2 per cent, further improves the hot-hardness.

(b) Cobalt added to the 18-4-1, 18-4-2, or 14-4-2 types further increases the hardness. The addition of more than 4 to 5 per cent cobalt is not effective in producing further increase in hot-hardness.

(c) No definite effect on the hot-hardness of commercial high-speed steels was found due to the addition of 0.5 to 1.5 per cent of molybdenum. The steels in which tungsten is wholly replaced by molybdenum have shown a somewhat lower hot-hardness.

4. Further data are needed to determine whether there is a correlation between the hot-hardness at 650° or 700° C. (1200° or 1290° F.) and the cutting efficiency of high-speed steels. Some data bearing on this phase of the investigation are presented in the next part of this study.

## PART II.—CORRELATION OF HOT-HARDNESS AND CUTTING EFFICIENCY OF HIGH-SPEED STEELS

The practical importance of this research on the hot-hardness of high-speed steels is obviously dependent upon a correlation of hot-hardness and cutting efficiency of the tools. The high-speed samples listed in Part I have not been subjected to cutting-efficiency tests.

Through the cooperation of T. G. Digges, of the U. S. Bureau of Standards, we were able to secure samples of many high-speed steel tools which had been used in various cutting-efficiency tests at the Bureau of Standards laboratory. These tools had been used in the cutting tests, and therefore were in the heat-treated condition. The tools were  $\frac{1}{2}$  by  $\frac{1}{4}$  in. in cross-section and varied in length from 2 to 4 or 5 in. By making a special compression block, it was possible to use specimens cut from these tools in hot-hardness tests. The tools were ground to 1-cm. diameter, thus affording a sufficient amount of circular area for the test. The length was the same as in the previous test. The composition and the results obtained in the tests are discussed in the following pages.

### *Mutual-indentation Hot-hardness of High-speed Steel Tools*

The compositions and heat treatments of the high-speed steel tools received from the Bureau of Standards are shown in Table 11, and the results of the hot-hardness tests are given in Table 12.

These steels may be grouped into four general classes. The 18-4-1 type is represented by AA, BB, E, I and E-22. Of these five steels, the Brinell hardness by the mutual-indentation method at 700° C. (1290° F.) averaged 175. The 14-4-2 type is represented by L, E-14, E-130 and E-97, although E-14 and E-130 have been modified by the

addition of about 3.75 per cent of nickel. In this group of steels the hardness at 700° C. (1290° F.) ranged from 145 to 215. The cobalt types of steels are represented by G, K and E-15. The hardness of these steels at 700° C. (1290° F.) was over 200 Brinell, except in E-15, when quenched from the low temperature of 2300° F. (1260° C.), which was only 180. Steel E-29 is a molybdenum steel, in which the tungsten is completely replaced by 7 per cent of molybdenum. The hot-hardness of this steel when quenched from 2400° F. (1315° C.) was only 170,

TABLE 11.—*Compositions and Heat Treatment of Tools from the U. S. Bureau of Standards*<sup>5,7,8,9</sup>

Steel No.	Chemical Composition							Hardening Temp. <sup>a</sup>	
	C	Cr	W	V	Co	Mo	Ni	°F.	°C.
AA	0.68	5.79	18.20	0.99	--	--	--	2400	1315
BB	0.70	5.68	17.60	1.18	4.5	--	--	2450	1345
E	0.62	5.95	17.86	0.68	--	--	--	2400	1315
G	0.59	5.25	18.51	1.17	5.45	--	--	2450	1345
H	0.66	2.99	12.67	1.74	--	--	0.18	2550	1290
I	0.65	5.97	18.88	0.81	--	--	0.15	2400	1315
K	0.60	2.95	18.23	0.99	5.50	--	0.09	2450	1345
L	0.71	5.60	12.75	1.99	--	--	--	2550	1290
E-14	0.69	5.64	13.75	1.92	--	--	5.70	2400 <sup>b</sup>	1315
E-15	0.76	5.75	15.55	1.99	5.68	--	0.22	2400 <sup>c</sup>	1315
E-22	0.61	5.66	17.40	1.02	--	--	5.71	2450 <sup>d</sup>	1345
E-29	0.71	4.74	--	0.54	--	7.07	--	2400 <sup>e</sup>	1315
E-97	0.64	5.41	15.02	1.99	--	--	--	2550	1290
E-150	0.61	5.94	15.05	1.90	--	--	5.81	2400	1315

<sup>a</sup> The steels were annealed 2 to 3 hr. at 1600° to 1625° F. (870° to 885° C.). The time at the hardening temperature was usually 1½ min., and the draws were usually 30 min. at 1100° F. (595° C.).

<sup>b</sup> Specimens also quenched from 2300°, 2350° and 2475° F. (1260°, 1290° and 1360° C.).

<sup>c</sup> Specimens also quenched from 2300° F. (1260° C.).

<sup>d</sup> Specimens also quenched from 2200° F. (1205° C.).

<sup>e</sup> Specimens also quenched from 2200° and 2450° F. (1205° and 1345° C.).

whereas when quenched from 2300° F. (1260° C.) it was 180, suggesting that possibly the hot-hardness is decreased by using the higher hardening temperature.

The effect of quenching temperature on the hot-hardness of these tools is further illustrated by the E-14, E-15 and E-22 samples. Steel E-14, when quenched from 2300° F. (1260° C.) had a hot-hardness of only 145, and this increased to 185 when the hardening temperature was 2475° F. (1360° C.). In the case of E-15, increasing the hardening temperature from 2300° to 2400° F. (1260° to 1315° C.) increased the hot-

hardness from 180 to 215. In the case of E-22 the hot-hardness of the specimens quenched from 2200° F. (1205° C.) was only 125, whereas when the specimen was quenched from 2400° F. (1315° C.) it was 165, but the value fell to 150 when the specimen was quenched from 2450° F. (1345° C.), again suggesting that there may be a maximum hardening temperature for maximum hot-hardness.

TABLE 12.—*Hot-hardness of High-speed Steel Tools<sup>a</sup>*

Steel No.	Hardening Temp.		Hardness by Mutual-Indentation Method				
	°F.	°C.	500°C. (570°F.)	400°C. (750°F.)	500°C. (930°F.)	600°C. (1110°F.)	700°C. (1290°F.)
AA	2400	1315	655	585	555	480	170
BB	2450	1345	640	615	570	520	190
E	2400	1315	655	600	575	490	170
G	2450	1345	655	600	585	505	215
H	2550	1290	615	610	570	485	215
I	2400	1315	640	600	575	505	180
K	2450	1345	655	610	570	515	205
L	2550	1290	655	610	555	485	215
E-14	2500	1260	625	555	520	580	145
E-14	2550	1290	655	560	515	415	170
E-14	2400	1315	655	550	515	415	180
E-14	2475	1360	610	555	505	395	185
E-15	2500	1260	655	610	560	475	180
E-15	2400	1315	670	610	570	500	215
E-22	2200	1205	555	505	455	285	105
E-22	2400	1315	625	585	525	395	165
E-22	2450	1345	660	555	525	415	150
E-29	2200	1205	655	610	570	480	150
E-29	2500	1260	645	625	585	480	180
E-29	2400	1315	---	610	555	455	170
E-97	2550	1290	655	610	570	505	180
E-180	2400	1315	640	555	520	415	205

<sup>a</sup> Samples received from U. S. Bureau of Standards

### *Correlation of Cutting Efficiency and Hot-hardness*

The various data published by Digges<sup>(5)</sup> and by French and Digges<sup>(7,8,9)</sup> have been compared with the hot-hardness values that have been determined on the high-speed steel tools received from the Bureau of Standards in studying the relations between the hot-hardness and cutting efficiency.

Table 13 shows the type of steel represented, the hardening temperature, the Taylor speed, cutting time, or tool life, together with the

hot-hardness at 600° and 700° C. (1110° and 1290° F.) for the tools that were used in one research by French and Digges.<sup>(7)</sup> The values shown for the cutting time or tool life are averages of six to eight tests, using three to four different tools and with about an equal number of tests after first and second grinds. There was considerable variation in the individual tests, and in extreme cases the minimum and maximum cutting time for tools of the same steel and the same heat treatment varied in the ratio of 1:2. As regards the Taylor speed, French and Digges calculated the values from the equation:

$$\text{Taylor speed} = \frac{\text{a constant}}{(\text{tool life})^{1/4}}$$

TABLE 13.—*Correlation of Hot-hardness and Cutting Efficiencies of High-speed Steels*<sup>a7</sup>

Sample No. b	Steel Types c	Hardening Temperature		Taylor <sup>d</sup> Speed	Cutting <sup>e</sup> Time	Hot-Hardness <sup>f</sup>	
		of °F.	°C.			600°C. 1110°F.	700°C. 1290°F.
E-15	Low W - Co	2400	1315	81.0	14.6	501	217
E-14	Low W - Ni	2475	1360	79.5	12.2	415	185
E-14	Low W - Ni	2400	1315	78.5	11.4	415	179
E-15	Low W - Co	2550	1290	78.0	11.1	475	178
L	Low W - High V	2550	1290	78	11.0	485	217
E-22	High W - Ni	2400	1315	74.5	7.4	598	165
I	High W - Low V	2400	1315	74	7.4	507	178
E-14	Low W - Ni	2500	1260	74	7.2	580	145
E-29	W replaced by Mo	2400	1315	72.0	5.9	456	169
E-29	W replaced by Mo	2500	1260	70.5	4.9	480	178
E-29	W replaced by Mo	2200	1205	69.0	4.2	480	152
E-22	High W - Ni	2200	1205	60.0	1.6	285	105

<sup>a</sup> Data on cutting efficiencies from French and Digges. Experiments with Nickel, Tantalum, Cobalt, and Molybdenum in High-speed Steel *Trans Amer Soc for Steel Treat.* (1925) 3, 681-699.

<sup>b</sup> Arranged in order of Taylor speeds

<sup>c</sup> See Table 11 for chemical compositions

<sup>d</sup> The speed required to cause failure in 20 minutes.

<sup>e</sup> Time before regrounding was necessary running at 85 ft. per min. with feed of 0.028 in. and  $\frac{3}{16}$ -in depth of cut

<sup>f</sup> Hot-hardness by mutual-indentation method.

and the figures given in Table 13 are their calculated values from the above equation. Since the average tool life was based upon six to eight tests and the Taylor speeds were calculated from the average tool life, the Taylor speeds may be said to represent the results of six to eight tests.

When the hardnesses at 600° C. (1110° F.) are plotted against the Taylor speed or the cutting time, a typical shotgun pattern is obtained. On the other hand, when the hardness values obtained at 700° C. (1290° F.) are plotted, there is a very definite trend, both when the hot-hardness is plotted against the Taylor speed and when it is plotted against the cutting time or tool life. These results are represented by the circles in Fig. 16. Bearing in mind the scatter mentioned above in the individual cutting times, as reported by French and Digges<sup>(7)</sup> and the resulting

scatter in the determinations of the Taylor speeds, it appears that rather good correlations are shown between the cutting efficiencies of these tools and their hot-hardnesses as determined by mutual indentation at 700° C. (1290° F.).

Specimen E-22 hardened at 2200° F. (1205° C.) shows significant results. The Taylor speed is 60, and the cutting time is 1.6 min., and the hardness at C. 700° (1290° F.) is 105. This indicates in a quite definite way that tools of such low hot-hardness are very poor in cutting efficiency. On the other hand, there is a rather general relation that the high Taylor speeds and the long cutting times are associated with the tools that have high hot-hardness properties.

Table 14 shows some results from another research by French and Digges<sup>(9)</sup> in which the high-speed steel tools were used in heavy cuts and in shallow cuts. These results are shown in Fig. 16. The same general relation holds, although for E-130, a low-tungsten high-vanadium steel with nickel, an unusually long cutting time was reported. Likewise, in the shallow cuts, steel E-97, a low-tungsten high-vanadium steel, showed a longer tool life than

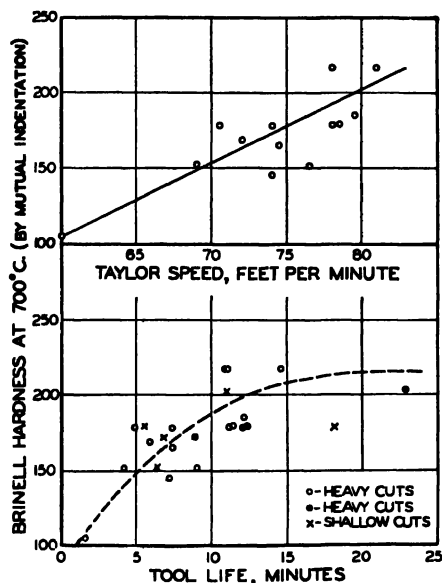


FIG. 16.—CORRELATION OF HOT-HARDNESS AND CUTTING EFFICIENCIES OF HIGH-SPEED STEEL TOOLS.

Solid circles represent heavy cuts; crosses, light cuts.

would be predicted from its hot-hardness of 180. As might be expected, these results indicate that there is some relation between the hot-hardness and the cutting efficiency of the tools, but they also indicate that other factors must be involved. In general, the effect of increasing the quenching temperature has resulted in an increase in the hot-hardness, as it is known to result in the increased cutting efficiency of high-speed tools. This is illustrated by E-14, E-15, E-22 and F-29 samples, as shown in Table 13.

Tools AA and BB were used by Digges<sup>(5)</sup> in his study on the Influence of Chemical Composition and Heat Treatment of Steel Forgings on Machinability with Shallow Lathe Cuts, but no comparative tests of these two tools were made.

Tools E, G, H, I and K were used by French and Digges<sup>(8)</sup> in their study on Rough Turning with Particular Reference to the Steel Cut, but

little use can be made of their data in attempting to correlate cutting efficiency and hot-hardness, because so few of their tests were made at the same speeds or on the same materials. Furthermore, the maximum range in the hardness at 700° C. (1290° F.) for these tools was only from 170 to 215. From their Table 8 a comparison of the Taylor speeds for tools E and G may be made, however. In a series of seven tests in which these two tools were used and in which steels varying in tensile strength from 85,600 to 135,500 lb. per sq. in. were cut dry, using a feed of 0.028 in. and a depth of cut of  $\frac{3}{16}$  in., the average Taylor speed for tool E was 58, while for tool G it was 64. The hardnesses of these tools

TABLE 14.—*Correlation of Hot-hardness and Tool Life of High-speed Steels*<sup>a</sup>

Sample No. b	Steel Types <sup>c</sup>	Hardening Temperature <sup>d</sup>		Cutting Time	Hot-Hardness <sup>e</sup>	
		°F.	°C.		600°C. 1110°F.	700°C. 1290°F.
Heavy cuts, 5/16 in. cut, .028 in. feed						
E-150	Low W - High V with Ni	2400	1315	22.9	415	205
E-14	Low W - Ni	2400	1315	12.5	415	179
E-97	Low W - High V	2550	1290	12.0	507	178
L	Low W - High V	2550	1290	11.0	485	217
E-14	Low W - Ni	2550	1290	8.9	415	172
Shallow cuts, .010 in. cut, .012 in. feed, and 330 ft/min.						
E-97	Low W - High V	2550	1290	18.2	507	178
E-150	Low W - High V with Ni	2400	1315	11.0	415	205
E-14	Low W - Ni	2550	1290	6.8	415	172
E-22	High W - Ni	2450	1345	6.4	415	182
E-14	Low W - Ni	2400	1315	5.5	415	179

<sup>a</sup> Data on cutting time from researches by French and Digges. *Trans. Amer. Soc. Mech. Engrs.* (1930) M.S.P. 52-56, 55

<sup>b</sup> Arranged in order of cutting time

<sup>c</sup> See Table 11 for chemical compositions

<sup>d</sup> Time before regrinding was necessary Results are averages of tests on five to eight tools

<sup>e</sup> Hot-hardness by mutual-indentation method

at 700° C. (1290° F.) by the mutual-indentation method were 170 for E and 215 for G, thus showing that the higher average Taylor speed was found for the tool having the higher hot-hardness, and it is significant that in each of the seven tests this relation was found.

In general, the high-speed tools from the Bureau of Standards were held  $1\frac{1}{2}$  min. at the hardening temperature, whereas the samples of high-speed steels listed in Table 9 were as a rule held 5 min. at the hardening temperature. The somewhat higher hardnesses observed on those specimens, as compared with the tools of similar composition received from the Bureau of Standards, would seem to indicate that a longer holding time at temperature results in a higher hot-hardness, but this point has not been extensively studied.



## PART III.—HOT-HARDNESS OF NITRIDED HIGH-SPEED STEELS

It is known that high-speed steels can be hardened by nitriding. It is also known that the nitrided cases produced on commercial nitriding steels retain relatively high room-temperature hardness after being heated to temperatures up to about 1000° to 1100° F. (540° to 600° C.). Therefore it appeared of interest to determine the hot-hardness of nitrided cases produced on high-speed steels.

Steels 22, 32, 38, 40 and 47 were selected and nitrided at temperatures from 1000° to 1110° F. (540° to 600° C.) for periods of about 50 hr. These nitrided specimens were then tested by the mutual-indentation method at temperatures of 600°, 700° and 800° C. (1110°, 1290° and 1470° F.). The results obtained were quite erratic and showed that the mutual indentation method of hardness testing is not applicable, as might have been suspected, to the determination of the hardness of comparatively thin cases. At the elevated temperatures the core softens somewhat, and in order to make a sufficiently wide impression for satisfactory readings on the surface of the case, it is necessary to apply a heavy load, which in some of the tests caused the cases to crack. In the interest of brevity of this paper, detailed results have been omitted.

## GENERAL DISCUSSION OF RESULTS

From the somewhat limited data available, there appears to be at least a first-order approximation to a correlation between the hot-hardness as determined by the mutual-indentation method and the cutting efficiency of high-speed steels. It is appreciated that the cutting efficiency of high-speed steels must depend upon a considerable number of factors. Undoubtedly, the strength and hardness of the matrix at the operating temperature are important factors. It is believed that the strength and hardness of the matrix are directly indicated by the hardness as determined by the mutual-indentation method. It should follow, therefore, that in cutting-efficiency tests in which the tool fails because such a high temperature has been developed that the failure results because of low hardness and strength of the matrix, there should be a very definite correlation between cutting efficiency and the hot-hardness.

The work to date indicates that 700° C. (1290° F.) is a critical temperature, but that a temperature of 650° C. (1200° F.) may be nearly as satisfactory. In cutting-efficiency tests in which the tool is not heated to a high temperature, it is hardly to be expected that the above-mentioned correlation will hold. The hot-hardness test will probably tell little or nothing as to whether or not the material has the proper amount and proper distribution of the carbide particles, both of which relations are known to be of importance in the performance of cutting tools. The hot-hardness test shows the effect of too low a quenching temperature,

which results in a low hardness value at the elevated temperatures, and there is some evidence that the hot-hardness falls off when an excessively high quenching temperature is used. The hot-hardness test applied to tools at 700° C. (1290° F.) differentiates the steels with reference to types. There is some indication that these types are classified in the order in which they will show maximum cutting efficiencies in types of service in which excessive temperature is developed. It has been found that air cooling, as compared with oil quenching, gives a much lower order of hot-hardness, and it is believed that this same relation may be found in cutting-efficiency tests, although data to prove this point are not available.

The hot-hardness curves of the high-speed steels as contrasted with those of materials of the Stellite type offer a reasonable explanation for the known superiority of the latter material in certain types of cutting tests.

If it can be shown that the hot-hardness tests by the mutual-indentation method when made at 700° C. (1290° F.) can be depended upon to predict cutting efficiency, this method may be used as a convenient way of determining the best alloy combinations to give high hot-hardness consistent with other desirable properties, and it may show that more economical combinations of our alloying elements are possible than are at present being used. For example, there is some indication that the efficiency of cobalt beyond 4 or 5 per cent in producing hot-hardness is very low. Such deductions, however, must be correlated with other methods of testing, because of the known importance of other factors than hot-hardness.

Finally, there is the possibility of a still wider application of this method of determining the hot-hardness of metals and alloys as a means of determining the suitability of materials for service at elevated temperatures and in selecting hot-working temperatures for metals and alloys.

#### ACKNOWLEDGMENT

The cooperation of the following companies in supplying materials aided greatly in conducting the study: Bonney-Floyd Co., Columbus, Ohio; Cleveland Twist Drill Co., Cleveland, Ohio; Columbia Tool Steel Co., Chicago Heights, Ill.; Crucible Steel Co. of America, Syracuse, N. Y.; Darwin & Milner Co., Cleveland, Ohio; Firth-Sterling Steel Co., McKeesport, Pa.; Halcomb Steel Co., Syracuse, N. Y.; Ludlum Steel Co., Dunkirk, N. Y.; The Midvale Co., Nicetown, Pa.; Bureau of Standards, Washington, D. C.; Vanadium Alloys Steel Co., Latrobe, Pennsylvania.

Thanks are also due to W. A. Welcker, Jr., A. F. Sprankle, and R. A. Karr, Dr. M. P. Benoy and C. F. Raab, of the Battelle staff, who assisted in various phases of the work. As previously stated, part of the work was done in cooperation with the Graduate School of Ohio State University, of which Prof. D. J. Demorest, of the Department of Metallurgy, was the representative and adviser.

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## DISCUSSION

*(F. N. Speller presiding)*

J. V. EMMONS, Cleveland, Ohio (written discussion).—This paper by Dr. Harder and Mr. Grove has potential usefulness to the industry. The critical summary of the previous work upon the subject, and their careful development of the selected method are both valuable. The conclusion reached that the hot-hardness is a considerable factor in determining the cutting efficiency of high-speed steels is of great interest. The correlation as shown in Fig. 16 is broad but is close enough to justify further work along this line.

An additional experiment has been performed through the courtesy of Dr. Harder for the purpose of comparing the hot-hardness of some of the molybdenum high-speed steels of the type discussed in the writer's paper on Molybdenum High Speed Steels, presented to the convention of the American Society for Steel Treating last October. The results upon four types of steels are presented in Table 15. The cutting efficiency

TABLE 15.—*Hot-hardness of Molybdenum High-speed Steels*

Steel	Composition, Per Cent					Hot-hardness, Brinell		Cutting Efficiency
	C	Cr	W	V	Mo	At 650° C	At 700° C	
A	0 84	3 51	1 42	0 98	8 83	380	169	108
B	0 65	3 60	18 29	0 95	None	337	152	100
C	0 79	3 55	None	1 00	10 72	304	152	91
D	0 75	3 91	4 19	1 12	8 17	277	160	64

estimates reported in this table are the result of drilling tests and are calculated in percentage of the performance of the 18-4-1 type of high-speed steel. All of the steels tested were hardened from the temperature that was found to give the maximum torsional strength, and were quenched in oil. These results are regarded as confirming the author's findings that there is some general relationship between the hot-hardness and cutting efficiency, but that there are other factors of great importance which sometimes cause a wide scatter of plotted points in such an analysis as in Fig. 16. The results are also regarded as furnishing additional evidence in confirmation of the opinion expressed in the paper on Molybdenum High Speed Steels referred to above to the effect that steels of type A have a higher cutting efficiency than that of previously known molybdenum steels such as type C; also that the addition of an excessive amount of tungsten to a molybdenum high-speed steel, as in type D, is deleterious. While the results of this additional experiment would seem to indicate that the testing temperature of 650° C. gives a better correlation with cutting efficiency than that of 700° C., it is believed that there is not yet available sufficient evidence to determine the point positively.

In general, it is believed that wider use of hot-hardness determinations will be found of interest and value. It is not expected that such methods alone will produce the final answer as to the cutting efficiency of unknown compositions or heat treatments. If they will only throw a little additional light from a new direction upon the subject of evaluating high-speed steels it will be worth while.

W. A. WISSLER and R. O. DAY, New York, N. Y. (written discussion).—Although the ability of a metal to retain its hardness while hot is a deciding factor in its suitability for use as a cutting tool or a wear-resisting surface, quantitative measurement-

of this property are comparatively rare in the literature, and the paper under discussion is a noteworthy addition to our knowledge of the subject. Without disagreeing in any way with the data given, we feel that the following information will be of interest.

When Stellite was introduced it was immediately noticed that it was superior to high-speed steel whenever the conditions of cutting were such that high temperatures were developed, and this fact, together with the knowledge that when cold it was softer than carbon or high-speed steel tools, led to the conclusion that it must have the property of retaining its hardness at high temperature. This was demonstrated years ago by unsuccessful attempts to forge or press the material while hot, and by applying a file to heated samples.

The first quantitative red-hardness tests on Stellite that have come to our attention were published in *Revue de Metallurgie* (July, 1918), by Guillet and Godfroid, who used the impact method on Stellite and high-speed steel. About 1925 we used the Rockwell machine for such determinations, and collected data comparing Haynes Stellite with high-speed steel. The results were not presented as a technical paper, but can be found in a discussion on page 725 of the A.S.S.T. *Transactions* for 1927. The experiments were made by heating the sample in a furnace, then removing it to a thermally insulated fixture and making Rockwell determinations as rapidly as possible. The curve, as published, gives Brinell hardness obtained by converting from Rockwell. A few years later it was thought that the Monotron would be more accurate, and a small furnace was built in which the sample could be heated and tested without removing it from the furnace. The data shown by Harder and Grove (p. 95) were obtained in this way, but the correction should be made that the indenter was not heated to sample temperature. Even this method, however, had errors, and the next step was to use the Monotron machine, but to use it as a diamond Brinell, measuring the temperature of the impression by projection on a ground glass by a metallurgical microscope. The results of these tests are not ready for release.

After having received notice some time ago of Dr. Harder's work we conferred with him, and built an attachment for a Brinell machine that is almost an exact duplicate of his. A few difficulties in securing consistent and accurate readings have been met, and at the present time we are not willing to say that it is necessarily more correct than the diamond Brinell method. It is admitted, of course, that a theoretical comparison of the two methods would lead one to believe that the mutual-indentation process would be more accurate, but our work has not progressed far enough to justify making any statement on this point.

We are interested in the point at which the curve for Haynes Stellite tools intersects the curve for high-speed steel. Samples 50-51 reported in Dr. Harder's work are Haynes Stellite. Tracing this point of intersection throughout his data we find that for the 18-4-1 steels the point is about 560° C., for the 18-4-5 it is about 615, and for the vanadium-free 18-4 steel listed it is 500° C.

The points of intersection taken from other work of this kind are 630° for Guillet and Godfroid (1918), 675° for Körber and Simonsen, 625 for our own work in 1925 as given in the A.S.S.T. *Transactions*, noted above, and 425 for our work as shown on page 95 of the paper by Harder and Grove, quoting from Grossmann and Bain, on high-speed steel.

The difference between our 1927 figures and those of other experimenters is due to one or more of several reasons. One is that the method itself differs, and although this would not be expected to change comparative readings, this point has not been determined. Our figures were based on samples of 18-4-1 available in 1927, and did not include any of the cobalt-bearing steels. The greatest difference, however, lies in the fact that the samples used by the various experimenters were held at the temperature indicated for different lengths of time. Guillet and Godfroid held the

sample 5 min.; Herbert completed the entire series in 3 hr., and our early work was done with a holding time of probably 10 min. Harder and Grove held the samples at temperatures for 20 min. A consideration of the subject, however, shows that inasmuch as the average life of a tool between grinds is several hours, the samples should be held at the desired temperature long enough to reach a point somewhere near their minimum hardness. A few experiments led us to select  $1\frac{1}{2}$  hr. as the most suitable holding period, and it can readily be seen that such a procedure is not only more rational in that it gives results more nearly like operating conditions, but also results in lower hardness figures for any metal that can be annealed at such temperatures.

As an indication of the effect of time, a few tests were made recently on an 18-4-1 cobalt high-speed steel using the mutual-indentation method and holding the samples for various periods of time. At  $700^{\circ}$  C. the samples held 20 min., 1 hr. and  $1\frac{1}{2}$  hr. had hardnesses of 275, which agrees with the results of Harder and Grove, 193 and 177, respectively. At  $600^{\circ}$  the hardnesses for 20 min. and  $1\frac{1}{2}$  hr. were 495 and 415, respectively, and at  $500^{\circ}$  the hardness after  $1\frac{1}{2}$  hr. holding was 575. Whether the effect of prolonged heating would be greater or less with cobalt-free steels has not been determined in our laboratory.

Stellite, on the other hand, is not affected by prolonged heating; hence if any of the other experimenters had used longer periods of time the net result would be to increase the slope of the steel curves and lower the temperature of equal hardness of Stellite and high-speed steel.

Various experimenters, including ourselves, have considered using red-hardness to evaluate cutting tools. Mr Herbert in 1927 suggested using a figure of merit based on the red-hardness of the tool and the maximum induced hardness of the metal being cut. For our part we have found that large differences in cutting quality can be detected by red-hardness measurements but there are several factors as yet not fully determined that must be investigated before accurate predictions can be made. For instance, there is considerable reason to believe that tools having different coefficients of friction will have different edge temperatures under the same cutting conditions. It is also likely that changes in the shape of the finished tool, such as clearance angles, side slope, etc., will affect the edge temperature. The temperature at which the hardness determinations is to be taken is, as pointed out by Harder and Grove, at present largely a matter of conjecture, and the time of holding is important. At the present time we feel that red-hardness should be investigated more fully with the belief that it will throw light on cutting tools, wear resistance, and high-temperature creep.

Our laboratories have a series of tests under way by which we hope to correlate much more closely than has been done red-hardness, tool life and cutting speed.

R. H. FRANK, Columbus, Ohio (written discussion).—While the writer is fully aware of the fact that the main purpose of this paper was a research on the hot-hardness of high-speed steels, several interesting facts are brought out by the results obtained on steels 50, 51 and 54, which could not be accurately classed as high-speed steels.

Referring to Fig. 15, the above-mentioned alloys show considerably higher hot-hardness values above about  $650^{\circ}$  C. and from Table 5 it can be seen that steels 50 and 51 have less tungsten than the majority of high-speed steels while 54 has more; furthermore, steels 50 and 51 are void of vanadium while 54 contains 1 per cent. On page 112 the authors say: "Tungsten, or possibly both tungsten and vanadium, are necessary to give good hot-hardness values." This statement may then account for the higher hot-hardness values of steel 54 but not 50 and 51. If cobalt, as the authors state on page 110, above 5 per cent does not contribute to hot-hardness values, the higher hot-hardness of steels 50 and 51 cannot be attributed to their high cobalt content, which is approximately 45 per cent. The carbon content of 50, 5

and 54 being considerably higher than the high-speed steels may, although the writer doubts it, have some influence, but then again this does not account for the superiority of 50 and 51 over 54, since they are essentially the same. This would narrow the reasoning for the superiority down to two reasons, the higher chromium content of steels 50 and 51 or the lower iron content (about 8 per cent as compared to 50 per cent in No. 54). From Fig. 5, which gives the hot-hardness of the component metals, it would not be amiss to assume that the higher iron content of steel 54 would contribute materially to its lower hot-hardness in comparison to Nos. 50 and 51, and may also be a reason why it shows superiority to high-speed steels (above  $650^{\circ}\text{C}$ ), since they contain more iron. Again, from Fig. 5 it can be seen that chromium shows the lowest rate in loss of hardness due to temperature, so this would leave the high chromium content (about 32 per cent), coupled with their low iron percentage, as the deciding factors in the superior hot-hardness of steels 50 and 51, over all the other alloys. The writer would like to ask if these deductions are in accord with the authors' views.

In their general discussion of results, the authors state (p 123) that "hot-hardness by the mutual-indentation method when made at  $700^{\circ}\text{C}$ . can be depended upon to predict cutting efficiency" Does this correlation hold when, instead of cutting, the service is one of severe abrasion at high temperatures? If it does, hot-hardness would be a direct method of measuring wear resistance at elevated temperatures

As is generally known, at room temperatures there is a fairly good correlation between Brinell hardness and tensile strength; that is, the hardness increases almost in direct proportion to the tensile strength, and this relation probably holds good at elevated temperatures.

Tapsell<sup>1</sup> says that there is no relation between ultimate stress at elevated temperatures and limiting creep stress at the same temperature; and doubts whether hardness values at elevated temperatures are of much value, but the writer would like to ask the authors if they hold the same opinion or if they think there is a relation between hot-hardness values and limiting creep stresses

T. G. Diggles, Washington, D. C. (written discussion).—The results given in Part II (p 116) on the correlation of hot-hardness with cutting efficiency are of particular interest to the writer, since the data on cutting tests are from several reports on work carried out by the writer and his associates in the Metallurgical Division of the Bureau of Standards.

The results given by Harder and Grove in Table 14 and reproduced in the lower part of Fig. 16 require some revision in order to avoid conclusions that may be misleading. The cutting tests with heavy cuts with steels E-130, E-14 and E-97, Table 14, were all made on the same forging at a speed of 100 ft. per min. The cutting tests with steel L were made on a different forging and at a different speed; namely, 85 ft. per min. The relation between the cutting speed and tool life for high-speed steel lathe tools has been shown to be represented by the equation  $VT^n = c$ , where  $V$  represents cutting speed;  $T$ , tool life;  $n$ ,  $\frac{1}{2}$  for roughing cuts and  $\frac{1}{10}$  for shallow cuts; and  $c$ , a constant. It is therefore obvious that the tool life obtained at a speed of 85 ft. per min. should not be compared with the tool life at 100 ft. per min. (all other cutting conditions being constant) without computing the results to a common basis. Furthermore, a comparison of tool performance is better made on a basis of the cutting speed for a selected tool life. The results of the tests with shallow cuts, as given in Table 14, were indeed made under similar cutting conditions and are comparable among themselves. However, the results of these tests as given in terms of tool life are not directly comparable with the results of the heavy cuts, as is indicated in Fig. 16.

<sup>1</sup> H. J. Tapsell: *Creep of Metals*, 137, 206. Oxford University Press.

In Fig 17 the Taylor speeds computed from the average tool life of the tests referred to above are plotted against Harder and Grove's Brinell hardness values at 700° C. In this series of tests with heavy cuts, the hot-hardness at 700° C. indicates the relative cutting qualities of the high-speed steel tools. This relation was not shown in the tests with shallow cuts.

Harder and Grove state that "Tools E, G, H, I and K were used by French and Digges in their study on Rough Turning with Particular Reference to the Steel Cut, but little use can be made of their data in attempting to correlate cutting efficiency and hot-hardness, because so few of their tests were made at the same speeds or on the same materials." This does not seem to the writer a correct estimate of the possibilities provided by the machinability data. It is, of course, to be expected that the writer should be more familiar than anyone else with these data and their possibilities. The following comparisons are therefore offered, not by way of criticism of the authors but in the hope that the additional comparisons may throw more light on the possibility of correlating hot-hardness with cutting efficiency of high-speed steel tools.

A comparison of the cutting quality of steels E, H, I, K, L and G may be obtained from the many cutting tests made with these tool steels.<sup>2</sup> The cutting tests were made with lathe tools with heavy cuts on plain carbon, chromium, chromium-vanadium, nickel, nickel-chromium, nickel-molybdenum and chromium-molybdenum steel forgings with tensile strengths between 65,000 and 195,000 lb. per sq in. From the results given in Table 7 and Fig 10 of the report in the *A S M E Transactions*, it can

be definitely shown that, for the test conditions under consideration, the Taylor speed in feet per minute for the different high-speed steel tools is approximately as follows:

$$I = L - 5 = K - 6 = H - 10 = E - 10 = G - 15$$

Furthermore, a consistent difference was shown in the cutting speeds of steels I and E, which was independent of the hardness or tensile strength of the steels cut. For example, if the cutting conditions were such as to give a Taylor speed at 50 ft per min with steel I, the approximate Taylor speeds of steels L, K, H, E and G would be of the order shown in Fig. 18. The hot-hardness values of the same steels as determined by Harder and Grove and reproduced in this figure permit comparisons of the cutting quality and

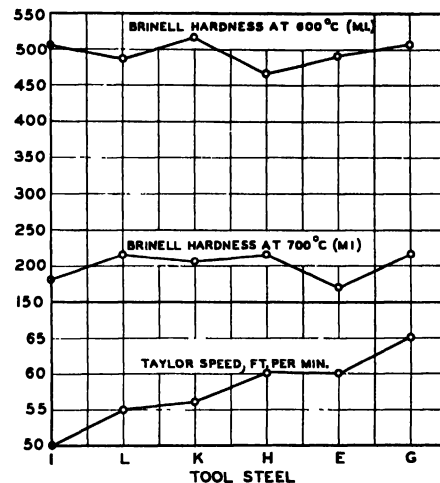


FIG. 18.—CORRELATION OF HOT-HARDNESS AND CUTTING QUALITY OF HIGH-SPEED STEEL TOOLS.

hot-hardness of the high-speed steels. The marked difference in the cutting qualities of the high-speed steels was not indicated by their hot-hardness values.

<sup>2</sup> Reported in *Trans. Amer. Soc. Mech. Engrs.* (1926) 48, 533.



Harder and Grove also state that "Tools AA and BB were used by Digges in his study on the Influence of Chemical Composition and Heat Treatment of Steel Forgings on Machinability with Shallow Lathe Cuts, but no comparative tests of these two tools were made." Fig. 19, which is from the results reported in the Bureau of Standards *Research Paper 319* (1931) gives the relation of Taylor speed to tensile strength of a nickel-chromium steel, S.A.E. 3435, cut with high-speed steel lathe tools containing different proportions of cobalt.

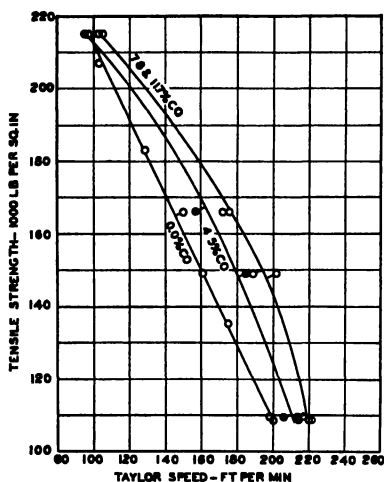


FIG. 19.—RELATION OF THE TAYLOR SPEED TO THE TENSILE STRENGTH OF A NICKEL-CHROMIUM (S.A.E. 3435) STEEL CUT WITH HIGH-SPEED STEEL TOOLS CONTAINING DIFFERENT PROPORTIONS OF COBALT.

The tool tests were made with shallow cuts. Steels AA and BB containing 0.0 and 4.5 per cent cobalt, respectively, were compared with steels containing 7.8 and 11.7 per cent cobalt. (Incidentally, it may be mentioned that the chemical analysis of steel BB given in Table 11 of Harder and Grove's report should also show 4.5 per cent cobalt.) The data show that lathe tool performance when cutting the steel forgings with tensile strength up to about 170,000 lb. per sq. in. was improved by the additions of cobalt (together with higher hardening temperatures) as compared with the customary 18 per cent tungsten type of high-speed steel. However, the increase in cobalt above about 5 per cent did not produce improvements of the same order as those resulting from 3.5 to 5 per cent. Similarly, Harder and Grove's hot-hardness tests show that 4 to 5 per cent cobalt added to the 18 per cent tungsten high-speed steel produced an increase in hot-hardness but the addition

of greater proportions of cobalt was not effective in increasing the hot-hardness; also the hot-hardness of steel BB was greater than that of steel AA.

A. B. KINZEL, New York, N. Y.—About a year ago we presented a report on the 18-4-5 type high-speed steel.<sup>3</sup> Shortly thereafter we arranged to supply Dr. Harder with specimens. The analysis of the material that was used is 18-4-5 with 1.4 per cent carbon. Work since then has shown that 18-4-5 with 1.5 per cent carbon gives still greater improvements. It is interesting to note that shop tests on the steels in question correlate with the hot-hardness data reported by Harder and Grove.

P. PAYSON, Harrison, N. J.—We have been making tests at an elevated temperature by an impact method substantially the same as that described in the paper under method B, and most of our work has been done on hot-worked steels of the chromium and chromium-tungsten type. Our Brinell values were determined from the impact impression by means of a conversion chart that we have made up, and our actual values compare fairly well with those presented in the paper for tests made at temperatures at below about 1000° F. At the higher temperatures, our values are considerably higher than those shown in the paper. For example, some of these high-speed steels are indicated to be about 45 to 60 Brinell when tested at about 1500° F., whereas our values show about 100 to 120. Those of us who are familiar with the working of high-speed steel realize that high-speed is pretty hard at forging temperatures, and it is a little surprising to see the value of 45 Brinell (which is com-

<sup>3</sup> A. B. Kinzel and C. O. Burgess: *Trans. A.I.M.E.* (1932) 100, 257-263.

parable to the hardness of annealed copper) as the hardness of high-speed steel at about 1500° F.

We have found with the hot-worked steels that air quenching as contrasted with oil quenching does not make any difference in the hot-hardness, providing the samples were tempered to approximately the same hardness. We did find that at temperatures below about 1000° F. the hardness was dependent upon the original hardness of the material. That is, a steel that started off at about 555 Brinell would have a greater hardness, regardless of the composition, when tested at 800 or 900, than the steel that started off at about 400 Brinell.

We found in this series of steels, which varied from about 3.75 per cent chromium steel to the higher priced type of tungsten-chromium hot-worked steels, starting with steels heat-treated to approximately the same hardness, 390 Brinell for one group and 450 Brinell for another, that all these steels tested at temperatures up to about 1000° F. had about the same hardness and that the superiority of the tungsten type showed up only when tests were made at temperatures higher than that. We found a definite relationship between increasing tungsten content and increasing hardness at a temperature of about 1200° or higher. So that there is good reason for the use of the higher tungsten type when the dies or tools are to be subjected to hot temperatures for a long time.

We found the time at temperature very important in determining the hardness of these hot-work steels, especially at the higher temperatures. In a series of tests we made at 1000° F. of samples that were held for  $\frac{1}{2}$  hr. to about 70 hr. at temperature, there was very little variation in hardness over that long period or among the different grades of steels, whereas when the tests were made at 1200° F. for a long period of time, some of the steels were definitely inferior to others. The higher tungsten steels maintained their hardness much better than the tungsten-free or low-tungsten type.

The suggestion that tests on tools for cutting purposes be made after various lengths of time at temperature is a good one. Obviously, cutting efficiency has a time factor in that the tool is held at temperature for some time while in service and some of these steels very likely have a greater resistance to softening with time at temperature than others. I think that would be a good way of distinguishing one grade from another.

**MEMBER**—Has there been any particular difficulty in treating the 18-4-5 tungsten high-speed steel type 140-150 carbon, and if so, what precautions are necessary in heat-treating it if 2350° is used for the final heat? Is either borax or some other medium used to prevent decarbonization?

**A. B. KINZEL**—Some who have handled the 18-4-5 one and one-half carbon type have said that they found it necessary to control the time of heating and temperature more closely than usual, whereas others just treat along with the regular high-speed steel and have no difficulty. As far as I know, borax has not been used, nor has it been found necessary. The tools, of course, are ground to shape after hardening and evidently any decarbonization that takes place is removed in the grinding.

**O. E. HARDER**.—Messrs. Wissler and Day have made a good point with reference to the time factor in making the hot-hardness tests. One is frequently limited in doing a piece of experimental work and cannot study all the variables that might well be studied. In our work, the specimens were at temperature about 20 min., and we believe that a longer time would make a considerable difference. As they have indicated, that difference would probably be in favor of the Stellite type of tools as compared with the high-speed steels. Obviously, the tests made by the impact method test a somewhat different property of the material from those made by the

usual Brinell or the mutual-indentation method. The results show the same general tendency, but the figures are not exactly equivalent.

We are entirely in agreement with Mr. Digges' idea that the heavy cuts are probably better for showing this correlation than the light cuts. It is obvious that in the heavier cuts, excessive temperature is more likely to develop in the cutting tool.

We are also appreciative of the suggestion made by Messrs. Wissler and Day about the coefficient of friction, and probably there are many other factors involved in the cutting efficiency of tools that will not be determined by hot-hardness tests. All we think you can make of the hot-hardness test is another way of determining the probable cutting efficiency or predicting the stability of the different steels at elevated temperature. It is just possible this method of testing has some application in determining the workability of steels of elevated temperatures. There is some difficulty in making tests up to temperatures that would correspond to the forging temperatures, although the tests should indicate the tendencies of the steel to soften at elevated temperatures if they are made up to 800° C (1470° F).

O. E. HARDER (written discussion).—The discussion and additional data by Mr. Emmons are appreciated. As he states, there appears to be a better correlation between the hot-hardness as determined by the mutual-indentation method and the cutting efficiency when the tests are made at 650° C (1200° F). It is possible that if a longer holding time at temperature, as suggested by Messrs. Wissler and Day, is employed a still lower temperature should be chosen for the hardness tests, in order to get the best indication of the cutting efficiency.

In reply to Mr. Frank's discussion and questions, our generalizations with reference to the presence of tungsten and vanadium being necessary to give high hot-hardness, and the efficiency of cobalt in greater amounts than 4 or 5 per cent, were intended to apply to high-speed steels only. It is hardly to be expected that these generalizations can be extended to such alloys as Nos. 50, 51 and 54. His suggestion that the higher iron content of No. 54 is an important factor in determining hot-hardness seems reasonable. The higher chromium and cobalt contents of samples 50 and 51 are probably important factors in contributing to their hot-hardness. It will be noted that sample 54 shows a more rapid loss in hardness as the temperature is increased, which suggests that 54 may soften somewhat on heating to elevated temperatures. Our data hardly justify predicting relative resistance to such complicated service as abrasion at elevated temperatures.

Our study has not included tensile or creep tests of high-speed steels. It may be added, however, that Page<sup>4</sup> has reported tensile tests on a high-speed steel containing C, 0.64; W, 13.4; Cr, 3.35; and V, 0.25 per cent. With what he considered correctly hardened specimens, the maximum strength-temperature curve is similar to our hot-hardness-temperature curve. As a matter of fact, the values from Page's data follow closely the character of the curve in our Fig. 11. We would not care to venture an opinion regarding a possible relation between hot-hardness by the mutual-indentation method and creep resistance.

Mr. Payson's observations seem to be in general agreement with our findings; that is, the differences in the steels are not evident until the tests are made at the higher temperatures, in the range of 1100° to 1250° F.

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<sup>4</sup> A. R. Page: Mechanical Properties of High-Speed Steel at Elevated Temperatures. *Metallurgia* (1930) 1, 239-241.

## The Precipitation-hardening of Copper Steels

BY CYRIL STANLEY SMITH\* AND EARL W. PALMER,\* WATERBURY, CONN.

(New York Meeting, February, 1933)

A COMPLETE discussion of the literature on the subject of the influence of copper on iron and steel will be published elsewhere.<sup>1</sup> The present paper is concerned especially with the precipitation-hardening of copper steels, and brief mention will be made here only of the work of Kinnear,<sup>2,3</sup> Nehl<sup>4</sup> and Buchholtz and Koster,<sup>5</sup> who alone have studied this phase of the subject.

Kinnear found that normalized low-carbon steel castings containing about 1.0 per cent copper on drawing at temperatures in the neighborhood of 530° C. (1000° F.) increased in tensile strength and yield point, with little decrease in ductility. The maximum effect was obtained with about 0.9 to 1.0 per cent copper, and when the copper exceeded 3 per cent no improvement occurred on reheating.

Kinnear did not study the effect of time of reheating—an all important factor where precipitation is concerned. Nehl,<sup>6</sup> who apparently was unaware of Kinnear's work, recognized the change as due to precipitation and studied the interdependence of time and temperature of reheating, the temperature of the initial solution heat treatment, and the speed of cooling necessary to retain the bulk of the copper in supersaturated solution and to give an increase in hardness and tensile strength on reheating. Nehl found that if the final rolling or forging temperatures exceeded 700° C. (1300° F.) it was not necessary even to normalize the steel, but full precipitation occurred on merely reheating the forged or rolled shapes at 500° C. (930° F.).

Buchholtz and Koster<sup>7</sup> studied in detail the precipitation-hardening of a mild steel containing 1.0 per cent copper and 0.5 per cent chromium. From data on the electrical and magnetic properties of copper steels, they drew the portion of the equilibrium diagram in Fig. 1, assuming the

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<sup>1</sup> Alloys of Iron Research Monograph on Alloys of Iron and Copper. In course of preparation

<sup>2</sup> Kinnear: U. S. Patent No. 1607086 (1926).

<sup>3</sup> Kinnear: *Iron Age* (1931) **123**, 696 and 820.

<sup>4</sup> Nehl: *Stahl und Eisen* (1930) **50**, 678.

Nehl: U. S. Patent No. 1835667 (1931).

<sup>5</sup> Buchholtz and Koster: *Stahl und Eisen* (1930) **50**, 687.

<sup>6</sup> References of footnote 4. <sup>7</sup> Reference of footnote 5.

resistance to be lineally dependent on the copper content in solution. This shows the solubility of copper in alpha iron to be 3.4 per cent at the eutectoid temperature 810° C. (1490° F.). There are many indications that the solubility is actually less than this, although the exact value has not been determined.<sup>8</sup>

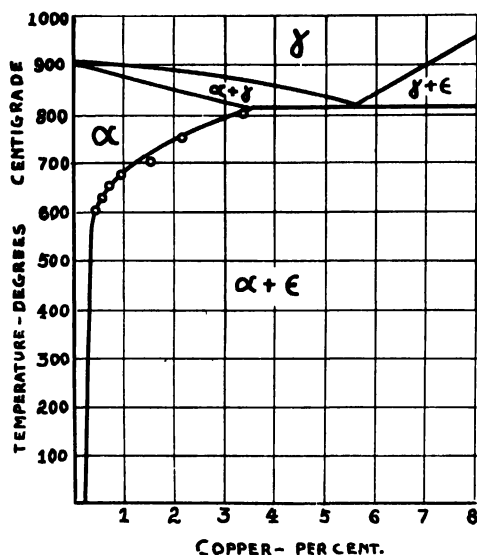


FIG. 1.—PORTION OF COPPER-IRON EQUILIBRIUM DIAGRAM (*Buchholz and Koster*).

Realizing that an important future for copper steels depends largely on this more or less unique property of precipitation-hardening, the authors made a detailed study of the phenomenon and its dependence on variations of treatment and composition. Most of the work described in the present paper is limited to simple ternary copper steels, although some preliminary results on quaternary steels containing copper have been obtained.

<sup>8</sup> The electrical conductivity of an alloy containing 0.91 per cent copper and 0.03 per cent carbon examined by the present authors was constant after quenching from any temperature above 760° C. (1400° F.) following heating for 24 hr., and it progressively increased as quenching temperatures lower than this were used. The eutectoid temperature was approximately redetermined by thermal analysis of an alloy containing 4.01 per cent copper, 0.011 per cent carbon, 0.068 per cent manganese, 0.026 per cent silicon. Cooling curves taken at the rate of 4° per minute showed an arrest at 824° C.; heating curves at 856° C. If the samples were held for prolonged times at temperatures between 824° and 840° C. and then cooled, the arrest at 824° C. would not appear, but heating for 3 hr. at 844° C. resulted in an arrest on cooling, and this temperature evidently was above that of the eutectoid. Approaching the change from the gamma field, transformation took place on holding for 1 hr. at 839° C. on cooling from 900° C., for the arrest at 824° C. then disappeared. The eutectoid temperature is placed by these experiments between about 840° and 844° C. (1544° and 1550° F.), but this temperature must be only provisionally accepted.

TABLE 1.—Influence of Speed of Cooling on Rockwell C Hardness of Copper Steels

Alloy No	Cooling Method		Ised KOH Quench	Oil Quench	Air Blast	Free Air	Sil-O-cel	In Copper Container	Furnace Cool	Controlled Furnace Cool	
	Average Cooling Time to 500° C.										
	Average Cooling Rate, Deg. C per Hr.										
Composition, Per Cent.	Reheated 4 Hr. Deg. C		ROCKWELL C HARDNESS, COOLED FROM 800° C								
	Cu	C									
861	1 05	0 028	- 9 5	- 12 8	- 9 4	- 11 8	- 12 1	- 13 2	- 6 2	- 0 8	- 4 3
862	1 06	0 038	+ 10 2	+ 8 5	- 8 8	+ 7 8	+ 10 2	+ 9 5	+ 9 8	+ 1 8	+ 0 1
863	1 07	0 048	- 14 1	- 14 2	- 13 4	- 15 0	- 13 8	- 21 0	- 7 8	- 1 8	- 2 8
864	1 08	0 058	+ 11 6	+ 8 9	+ 9 4	+ 11 7	+ 2 0	+ 10 0	+ 8 4	+ 2 4	+ 0 6
865	1 09	0 068	46 0	10 9	4 4	4 0	17 6	16 1	15 1	12 2	0 4
866	1 10	0 078	33 7	20 9	18 0	18 6	17 6	16 1	15 1	12 2	0 4
867	1 11	0 088	58 0	20 5	16 0	11 3	20 2	18 4	15 1	12 2	0 4
868	1 12	0 098	38 7	25 6	24 7	21 4	20 2	18 4	15 1	12 2	0 4
869	1 13	0 108	63 8	28 1	20 4	15 6	12 4	13 3	15 1	12 2	0 4
870	1 14	0 118	39 9	29 6	24 5	22 6	25 5	20 4	15 8	11 4	5 3
871	1 15	0 128	64 2	50 7	34 9	29 2	28 5	23 2	19 7	15 8	10 7
872	1 16	0 138	42 3	41 0	36 6	32 6	30 2	29 0	26 2	20 4	13 1
873	1 17	0 148	- 4 5	- 6 1	- 6 2	- 4 0	+ 0 1	- 3 0	- 10 5	- 9 6	- 14 8
874	1 18	0 158	+ 17 6	+ 15 5	+ 13 5	+ 17 3	+ 14 3	- 14 7	+ 10 5	- 11 0	- 12 2
875	1 19	0 168	0 0	- 0 2	- 1 1	- 0 5	+ 2 8	- 0 7	- 10 5	- 13 2	- 10 4
876	1 20	0 178	21 3	+ 20 9	+ 18 7	+ 16 4	+ 15 8	+ 13 8	+ 10 0	- 10 9	- 6 4
877	1 21	0 188	20 3	5 8	2 3	2 1	4 0	1 5	2 4	+ 3 7	- 3 6
878	1 22	0 198	27 0	23 1	20 2	18 6	16 6	14 4	16 1	+ 0 0	- 5 5
879	1 23	0 208	39 0	11 7	10 2	7 4	6 9	5 2	2 8	- 5 0	- 1 9
880	1 24	0 218	34 2	28 0	23 1	19 0	17 1	14 9	12 3	12 4	- 7 6
881	1 25	0 228	63 0	37 2	29 4	25 1	20 3	20 4	15 3	13 9	- 8 7
882	1 26	0 238	41 7	39 0	35 8	29 5	25 2	25 3	20 0	1 3	- 3 8
883	1 27	0 248	46 4	29 1	18 4	14 2	11 4	7 2	4 1	2 4	- 2 0
884	1 28	0 258	37 3	31 1	27 3	20 3	18 2	15 7	11 3	4 7	- 2 0
885	1 29	0 268	65 0	31 8	21 9	13 4	9 3	9 0	7 8	5 6	- 0 4
886	1 30	0 278	37 0	29 3	20 8	14 0	10 3	9 4	8 6	3 6	- 0 4
887	1 31	0 288	31 4	26 1	19 6	13 0	10 0	9 3	6 4	3 6	- 0 4

\* Not reheated. Hardness measured directly after cooling.

\* Reheated 4 hr. at 450° C. Maximum hardness

FIG 2  
No 861. 1.05 % Copper, 0.020 % Carbon

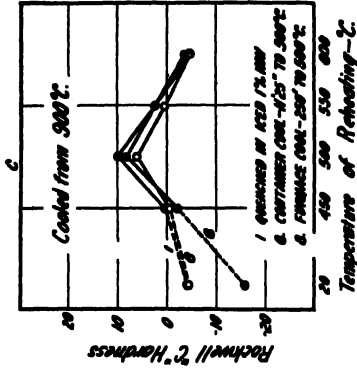
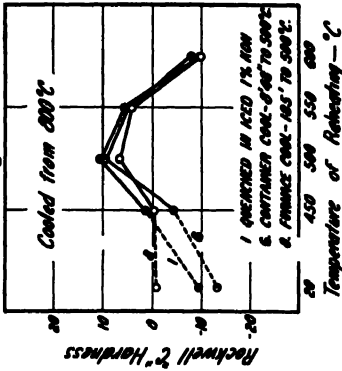
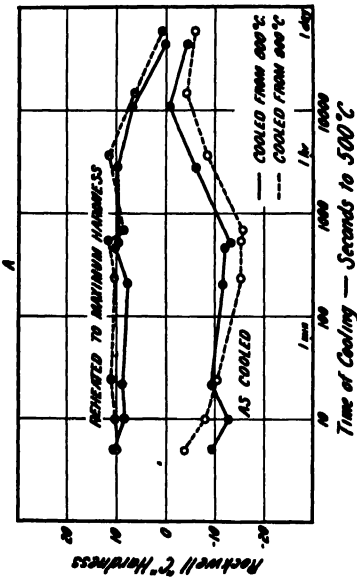


FIG 3  
No 856. 1.05 % Copper, 0.217 % Carbon

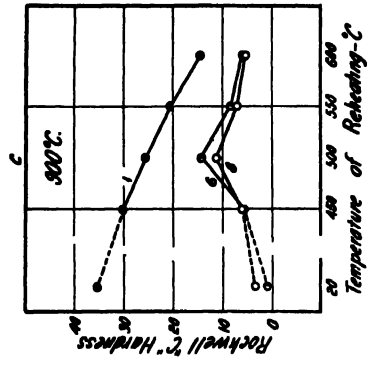
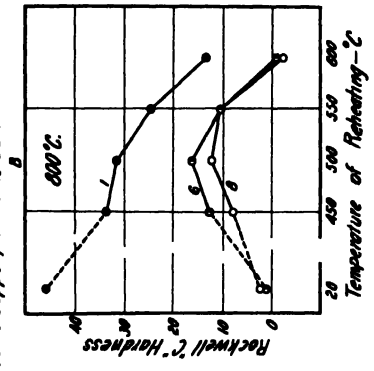
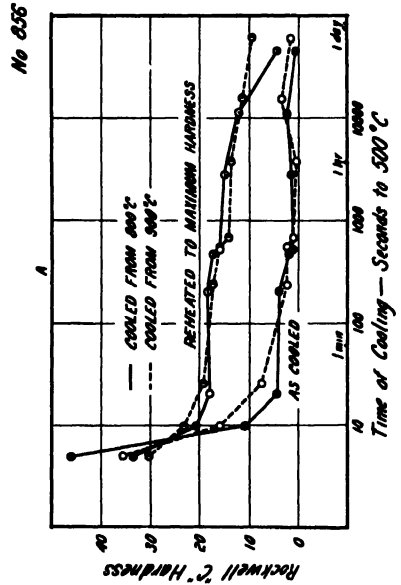
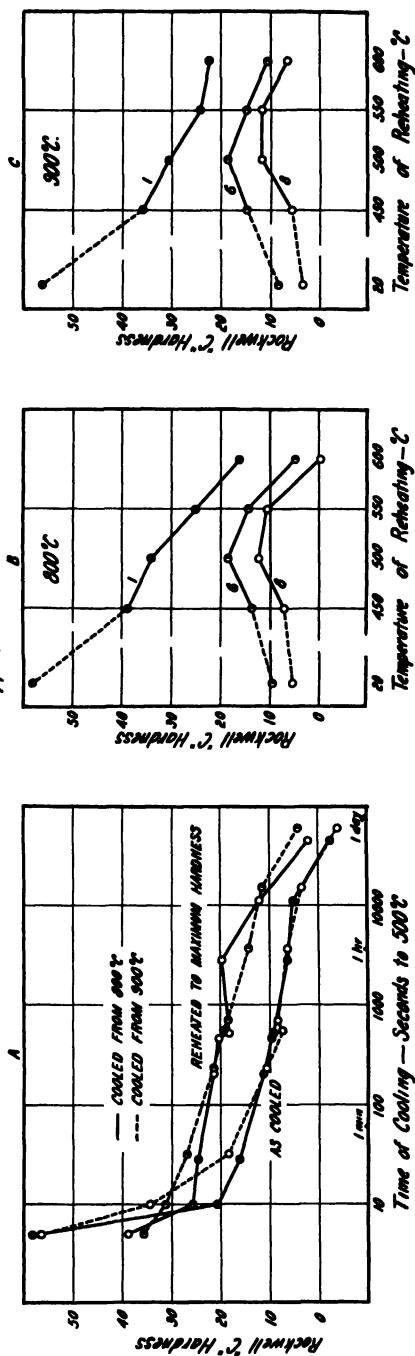


FIG. 4  
No. 854: 1.03% Copper, 0.458% Carbon



FIGS. 2-4.—COOLING-RATE STUDIES ON COPPER STEELS.

A. Influence of time of cooling.

B. Influence of reheating temperature on hardness of steels cooled at various rates from 800°C.

C. Influence of reheating temperature on hardness of steels cooled at various rates from 900°C.

Unlike carbon steels, which harden on quenching, copper-iron alloys subject to precipitation-hardening are softest in the quenched condition, and harden on heating at an intermediate temperature that would soften a quenched carbon steel. According to the current theory of precipitation-hardening, the effect is due to the copper, retained in metastable solid solution by rapid cooling, being thrown out of true solution into a critically dispersed form (which may or may not be a true precipitate) on reheating to a temperature that confers sufficient atomic mobility to allow the change to take place. Heating at too high a temperature or for too long a time results in softening, due to the growth of the copper particles to a size too large to have much hardening effect. Both time and temperature of treatment must therefore be considered of equal importance.

To determine the influence of speed of cooling from the solution heat treatment, samples of several alloys were



cooled from both 800° and 900° C. (1475° and 1650° F.) at nine different rates. Hardness measurements were taken and the specimens then reheated at various temperatures to determine the extent of precipitation-hardening following the various cooling rates. A selection from the mass of data obtained is given in Table 1 (cooling from 800° C. only) and plotted in Figs. 2 to 4.

Cooling through the precipitation range at a rate exceeding about 25° C. (45° F.) per minute suffices to keep in solution 1 per cent copper in a low-carbon steel; and, while precipitation-hardening occurs during cooling at a slower rate than this, the final hardness after reheating is not greatly affected until the rate is less than 1.5° C. per minute (2.7° F. per minute) and some hardening occurs even after cooling at 0.4° C. per minute (25° C. or 45° F. per hour). The presence of carbon renders the alloys more sensitive, causing the hardness to decrease with decreasing cooling rate as well as slightly reducing the extent of hardening due to reheating, and, in the case of the quenched steels, resulting in actual softening on reheating. Nevertheless, even in high-carbon alloys, precipitation will occur to a useful extent following cooling at a rate of 1.5° C. per minute (100° C. or 180° F. per hour) and is not absent after cooling at 25° C. (45° F.) per hour.

The importance of this will be realized. To obtain the best properties from copper steels *it is not necessary to quench*. An air cool, even of comparatively heavy sections, suffices to retain most of the copper in solution and to result in a considerable increase in hardness when the simple precipitation treatment is given.

#### TENSILE PROPERTIES OF COPPER STEELS

The influence of cooling rate having been studied, the mechanical properties of a large series of steels with varying carbon and copper contents were next determined. All the steels were normalized and a limited number were furnace-cooled and quenched from two different temperatures. Tensile tests were performed after these treatments and after the steels had been given the standard precipitation treatment (4 hr. at 500° C., 930° F.). The steels for these studies were 12-lb. heats made in magnesia crucibles in a small high-frequency furnace. The melts were deoxidized with silicon and manganese, the residual amounts being about 0.5 per cent manganese and 0.05 per cent silicon in the low-carbon heats, 0.10 to 0.15 silicon in the others. Final killing was with 0.025 per cent aluminum, added in the form of wire plunged to a pre-determined depth. The copper and carbon contents were very close to the desired value. All ingots, which were cast with a hot top of sufficient size, were forged to rods ¾-in. diameter and normalized before testing. The forging temperature was kept below the melting point of copper to avoid surface checking.

## NORMALIZED STEELS

To obtain tensile data on the effect of normalizing temperature, a steel containing 1.01 per cent copper and 0.108 per cent carbon was normalized at temperatures between 700° and 950° C. (1290° and 1740° F.)

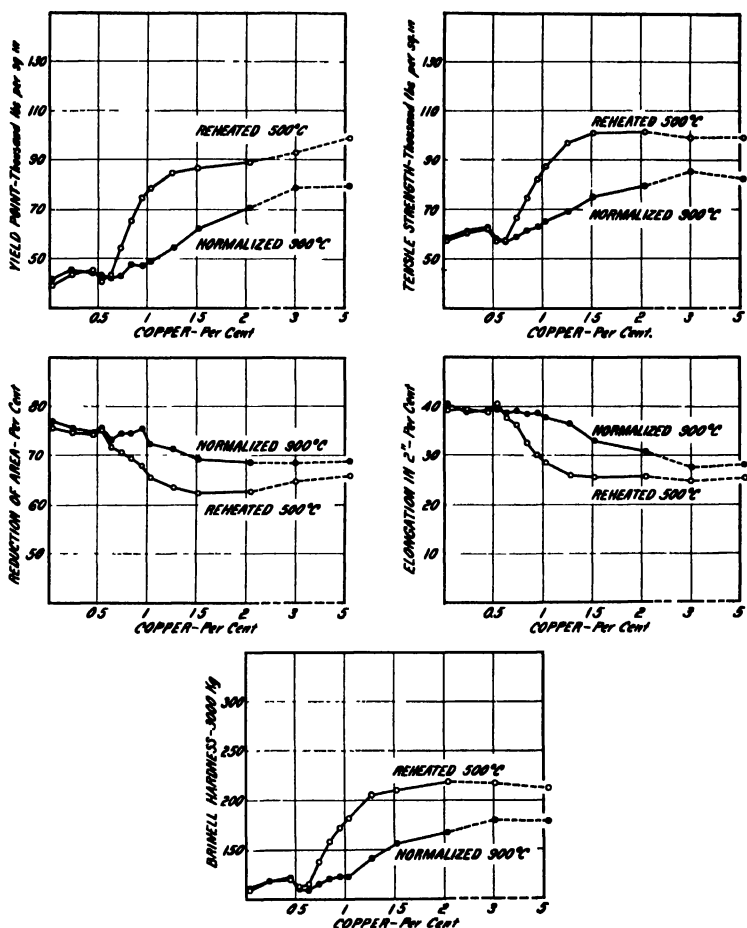


FIG. 5.—INFLUENCE OF COPPER CONTENT ON MECHANICAL PROPERTIES OF 0.05 TO 0.08 PER CENT CARBON STEELS.

Normalized from 900° C. and reheated 4 hr. at 500° C.

and tested both in the normalized condition and after reheating for 4 hr. at 500° C. (930° F.) following the different normalizing treatments, which were of one hour's duration. The results of the mechanical tests are as shown in Table 2. There is evidently little to gain by exceeding 800° C. (1475° F.) as a normalizing temperature, and even 750° C. (1380° F.) is sufficient to give almost maximum precipitation; 700° C. (1290° F.) is too low to result in much copper being dissolved.

A series of hardness tests on several steels showed that at 800° C. (1475° F.) 30-min. treatments sufficed to dissolve most of the copper, while after 1 hr. no further change occurred. At 950° C. (1740° F.)  $\frac{1}{2}$  hr. proved to be ample. All normalizing treatments referred to later were of one hour's duration at the temperature stated.

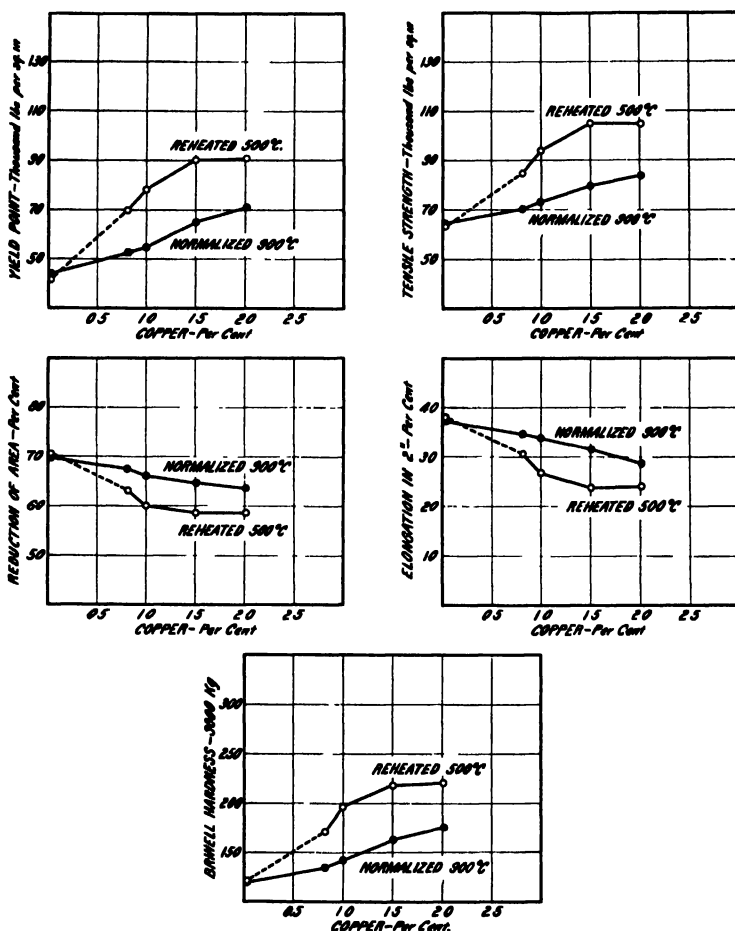


FIG. 6.—INFLUENCE OF COPPER CONTENT ON MECHANICAL PROPERTIES OF 0.12 PER CENT CARBON STEELS.  
Normalized from 900° C. and reheated 4 hr. at 500° C.

In Figs. 5 to 9 are plotted the tensile properties of the five main series of steels, each with constant carbon content and copper from 0 to 3 or 5 per cent, after normalizing and after normalizing and reheating for 4 hr. at 500° C. (930° F.).

In the normalized 0.05 to 0.08 per cent carbon series (Fig. 5), copper up to 3 per cent causes a steady increase in yield point and tensile strength,

TABLE 2.—*Influence of Normalizing Temperature on Properties of Copper Steel*

Alloy 919: 1.01 per cent copper, 0.108 per cent carbon

Normalising Temperature		Yield Point, Lb. per Sq. In. (0.5 Per Cent Extension)	Tensile Strength, Lb. per Sq. In	Elongation, Per Cent on 2 In.	Reduction of Area, Per Cent	Brinell Hardness
Deg. C.	Deg. F.					
PROPERTIES AS NORMALIZED						
700	1290	54,200	69,700	35 0	71 0	138
750	1380	53,600	70,700	35 5	68 9	139
800	1470	54,900	71,100	34 5	68 3	138
850	1560	52,200	71,100	35 0	67 0	142
900	1650	55,400	70,900	35 0	67 5	141
950	1740	53,200	70,200	35 0	67 3	140

PROPERTIES AFTER REHEATING 4 HR. AT 500° C.

700	1290	60,700	72,200	31 0	69 8	149
750	1380	74,100	90,900	28.5	62 6	189
800	1470	78,200	92,000	28.0	61 9	195
850	1560	79,500	93,300	28 0	61 2	198
900	1650	77,500	94,300	27 0	60 4	197
950	1740	81,100	93,900	27 0	59 8	198

TABLE 3.—*Increase in Yield Point and Tensile Strength Due to Precipitation-hardening of Normalized Copper Steels\**

1.0 Per Cent Copper			1.5 Per Cent Copper		
Percentage of Carbon	Increase in		Percentage of Carbon	Increase in	
	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.		Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.
0.028	35,800	26,900			
0.038	35,100	25,100			
0.071	29,800	22,300	0.075	24,100	25,750
0.108	23,300	20,900			
0.132	23,450	20,550	0.133	25,000	25,050
0.203	25,450	21,900	0.202	20,400	22,600
0.269	28,150	22,200	0.269	21,650	21,650
0.459	24,950	19,600	0.407	19,300	17,750
0.56	20,150	17,800			
0.898	19,150	8,800			

\* These figures are in addition to the increase in base properties due to the addition of copper without precipitation treatment—about 10,000 lb. per sq. in. for 1.0 per cent, 15,000 lb. per sq. in. for 1.5 per cent copper steels.

with a steady but small decrease in ductility. The 5 per cent copper steel has about the same properties as that with 3 per cent copper. The slight variations in the low-copper steels are due to small variations in the carbon and manganese content.

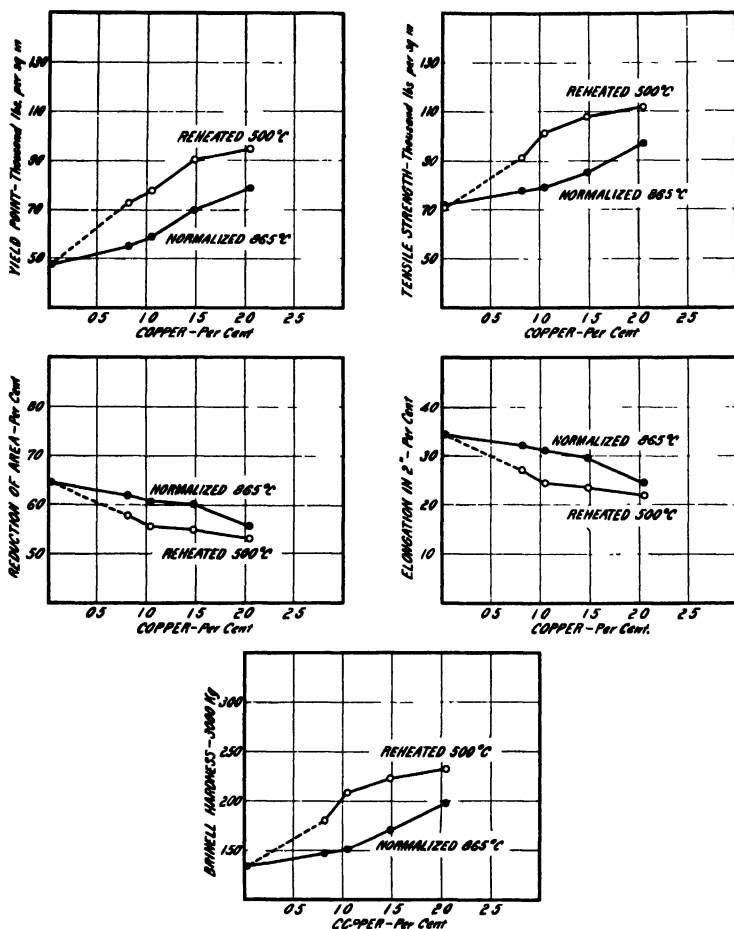


FIG. 7.—INFLUENCE OF COPPER CONTENT ON MECHANICAL PROPERTIES OF 0.20 PER CENT CARBON STEELS.

Normalized from 865° C. and reheated 4 hr. at 500° C.

Reheating for 4 hr. at 500° C. (930° F.) causes no change in the alloys containing up to 0.63 per cent copper, but with 0.74 per cent copper there is a distinct increase in yield point, tensile strength and hardness, accompanied by a small decrease in elongation and reduction of area. With more copper the increase due to precipitation is greater, reaching a maximum change in the yield point of 30,000 lb. per square inch at about 1.25 per cent copper, although the actual values of the properties continue to increase up to 5 per cent copper.

The same type of curve is obtained for the influence of copper in the four series with higher carbon contents (Figs. 6 to 9), although the curves are displaced by the higher base properties. Carbon reduces the extent of the improvement in tensile strength due to precipitation, and, to a smaller extent, the increase in yield point. This effect is well shown by Fig. 10 and Table 3.

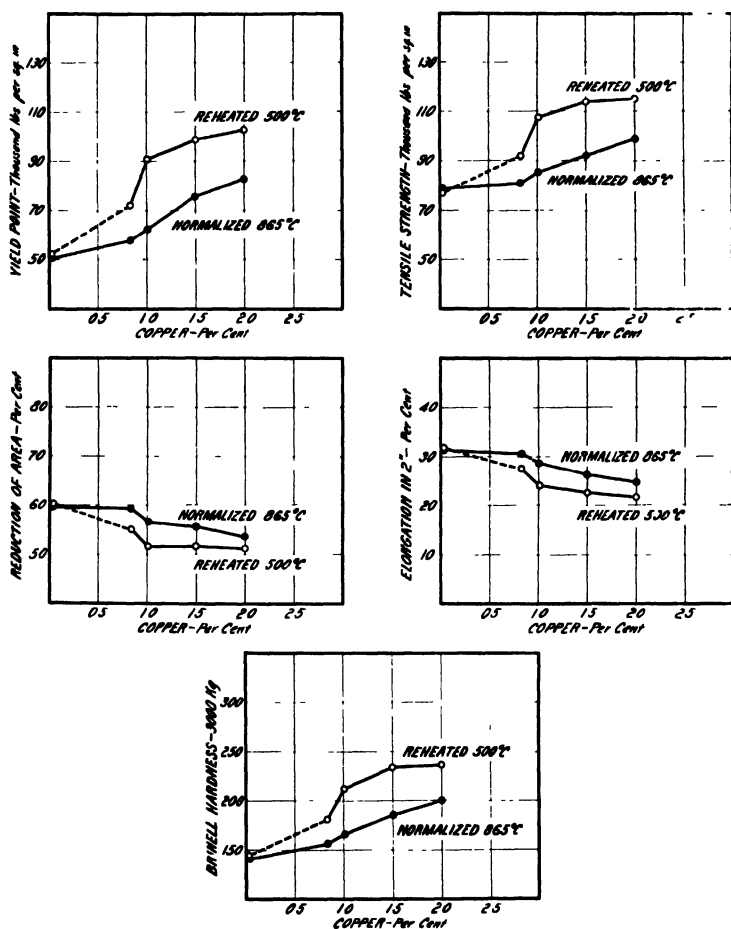


FIG. 8—INFLUENCE OF COPPER CONTENT ON MECHANICAL PROPERTIES OF 0.27 PER CENT CARBON STEELS.  
Normalized from 865° C. and reheated 4 hr. at 500° C.

### QUENCHED COPPER STEELS

The effect of quenching temperature on three high-copper alloys of low carbon content was studied, with the results shown in Fig. 11. Quenching from 800° C. (1475° F.) rendered all three alloys in the softest state, some copper being in solution in alpha iron and the excess spheroid-

ized and having little effect on the hardness. Reheating at 500° C. precipitated the copper from the alpha solution, and increased the hardness by an amount about the same as a 1.5 per cent copper alloy quenched from the same temperatures. Above the eutectoid temperature (843° C.) larger amounts of copper go in solution and increase the hardness of the

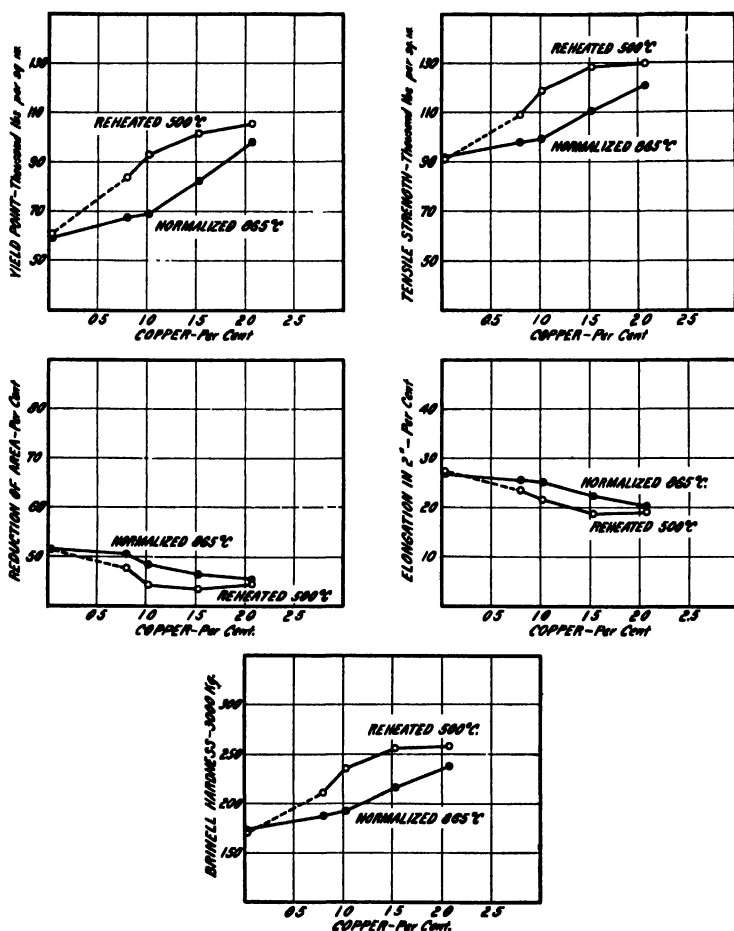


FIG. 9.—INFLUENCE OF COPPER CONTENT ON MECHANICAL PROPERTIES OF 0.43 PER CENT CARBON STEELS.  
Normalized from 865° C. and reheated 4 hr. at 500° C.

quenched alloys. On account of the sloping  $\gamma$  boundary the hardness continues to increase up to 900° C. (1650° F.) for the 2 per cent alloys, and 950° C. (1750° F.) for the 4 per cent alloy, while the 7 per cent alloy continues to increase up to 1190° C. (2175° F.).

Figs. 12 and 13 show the hardness of alloys with 0.03 per cent carbon and up to 9.3 per cent copper (forged up to 7.74 per cent copper, cast

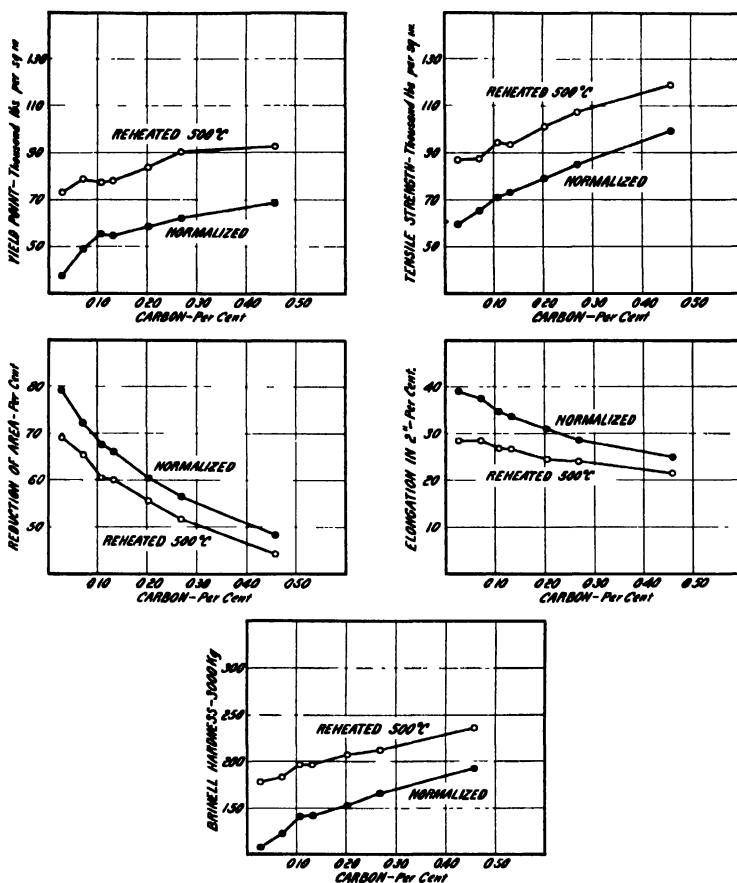


FIG. 10.—INFLUENCE OF CARBON CONTENT ON MECHANICAL PROPERTIES OF NORMALIZED AND REHEATED STEELS CONTAINING 1.02 PER CENT COPPER.

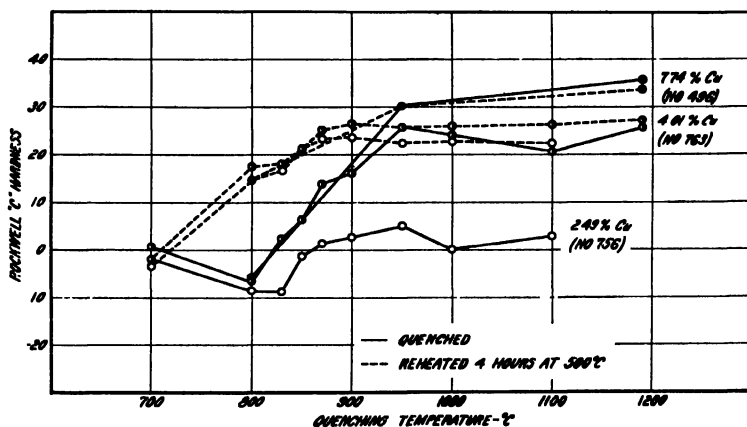


FIG. 11.—INFLUENCE OF QUENCHING TEMPERATURE ON HARDNESS OF COPPER-IRON ALLOYS, QUENCHED IN WATER AND REHEATED 4 HR. AT 500° C.



8.57 and 9.33 per cent) quenched from 800° and 950° C. (1475° and 1740° F.) and also reheated for 4 hr. at 500° C. (930° F.).

The high-copper alloys undoubtedly decompose entirely to the alpha form during quenching from above the critical point, and their hardness may be due either to a true supersaturated solution of copper in the body-

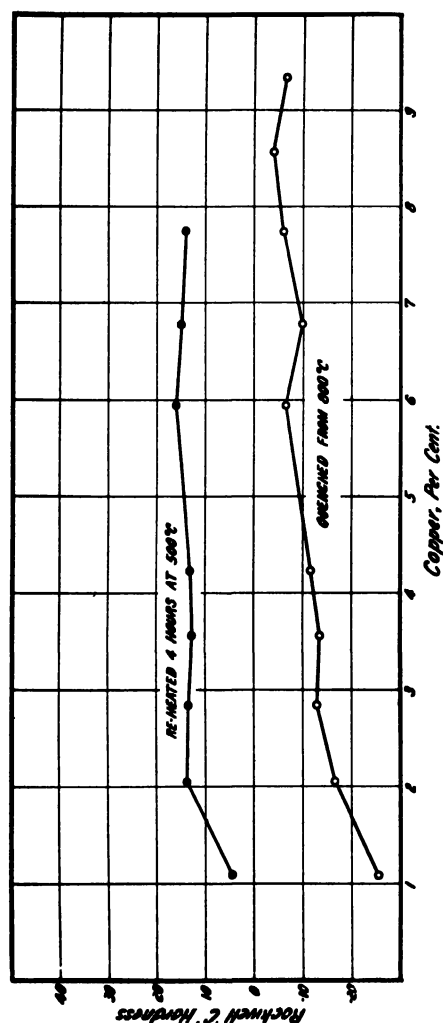


FIG. 12.—INFLUENCE OF COPPER CONTENT ON HARDNESS OF IRON-COPPER ALLOYS, QUENCHED IN WATER FROM 800° C. AND REHEATED 4 HR. AT 500° C.

centered cubic lattice or to a dispersion of the copper in some stage of precipitation. The absence of a "martensitic" form of decomposition is doubtless due to the fact that the copper atoms form a substitutional rather than interstitial type of solid solution in the gamma lattice, and no diffusion is necessary in changing from the face-centered to the body-centered cubic structure.

Test pieces of all the alloys in the series with 0.05 to 0.08 per cent and 0.20 per cent carbon were oil-quenched from 800° C. (1475° F.), the first series also from 950° C. (1740° F.) and the latter from 900° C. (1650° F.). The results are plotted in Figs. 14, 15 and 16. Oil quenching does not retain the 0.20 per cent carbon steels in the martensitic condition, and the effect in each case is mainly due to copper. The properties after quenching from 800° C. (1475° F.) are not greatly different from the normalized specimens (Fig. 14). From 950° C. (1740° F.)

(Fig. 15) solution of larger quantities of copper above the eutectoid temperature results in an increase of yield point and tensile strength with increasing copper content, both in the quenched condition and after precipitation treatment, though the change due to precipitation becomes steadily less as the copper increases, and there is an actual decrease in the 5 per cent copper alloy.

The properties of high-carbon steels in the quenched condition were, unfortunately, not studied in much detail, although precipitation offers an excellent means of maintaining high tensile strength and yield point while increasing the ductility by drawing at high temperatures.

### FURNACE-COOLED STEELS

It has been shown above that cooling at a rate as slow as  $100^{\circ}\text{C}$ . ( $180^{\circ}\text{F}$ .) per hour does not entirely remove the capacity for precipitation-hardening on reheating. To obtain definite tensile data on this, samples from the 0.05 to 0.08 and 0.20 per cent carbon series were furnace-cooled at this rate from  $800^{\circ}\text{C}$ . ( $1475^{\circ}\text{F}$ .) and tested both in this condition and after the standard reheating treatment. Figs. 17 and 18 show the results obtained, plotted against copper content.

### THE PRECIPITATION HEAT TREATMENT

The several variations of solution heat treatment described above were followed by a precipitation heat treatment consisting of heating for 4 hr. at  $500^{\circ}\text{C}$ . ( $930^{\circ}\text{F}$ .). This was adopted, after a complete study of the effects of variations of time and temperature, as representing the best compromise between a very long treatment at low temperatures, which gave the best properties, and a very short treatment at higher temperatures. Figs. 19 and 20 show the change in Brinell hardness of two normalized steels on reheating in a salt bath at temperatures between  $450^{\circ}$  and  $600^{\circ}\text{C}$ . ( $840^{\circ}$  and  $1110^{\circ}\text{F}$ .) The curves are typical of any precipitation-hardening alloy, showing a rapid increase followed by a flat maximum

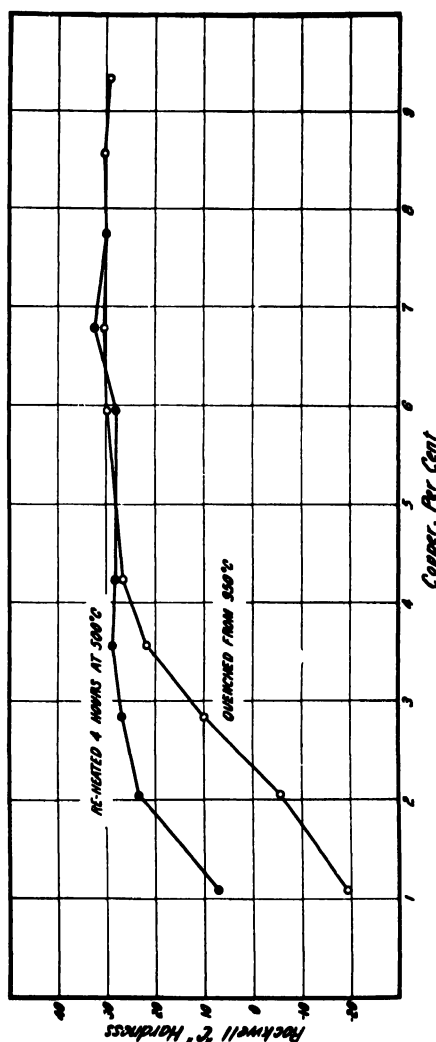


FIG. 13.—INFLUENCE OF COPPER CONTENT ON HARDNESS OF IRON-COPPER ALLOYS, QUENCHED IN WATER FROM  $950^{\circ}\text{C}$ . AND REHEATED 4 HR. AT  $500^{\circ}\text{C}$ .

and slow decrease. At 600° C. (1110° F.) maximum hardness is obtained in 15 min., while at 450° C. (840° F.) a somewhat greater hardness is attained, but only after 18 to 32 hr. heating. There is a definite incubation period in the lower temperature series. Table 4

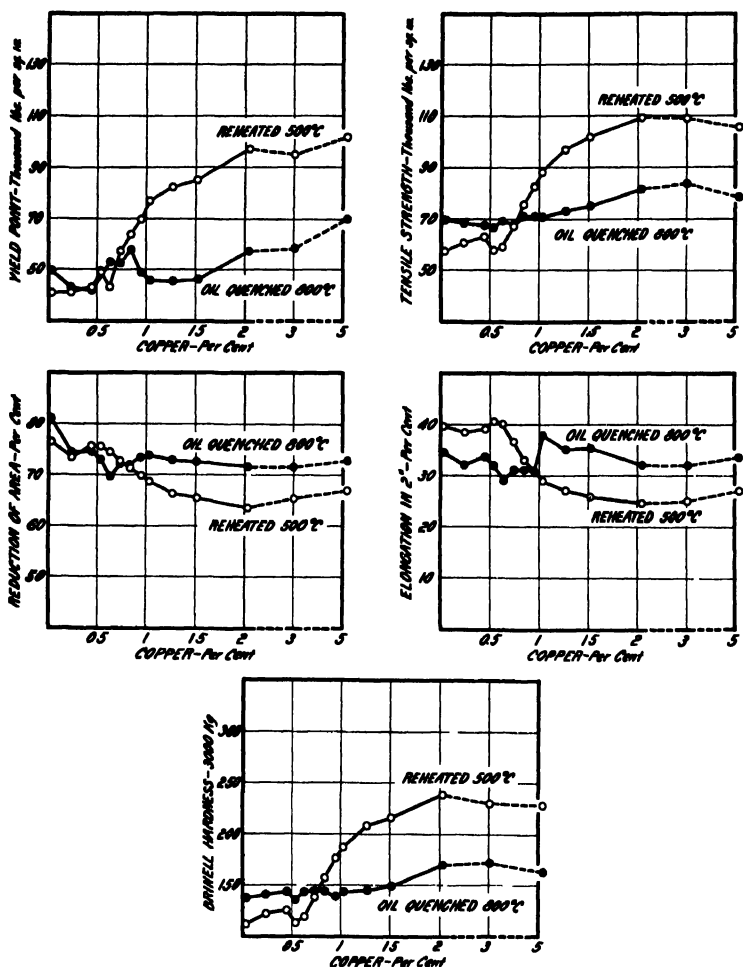


FIG. 14.—INFLUENCE OF COPPER CONTENT ON MECHANICAL PROPERTIES OF 0.05 TO 0.08 PER CENT CARBON STEELS, QUENCHED IN OIL FROM 800° C. AND REHEATED 4 HR. AT 500° C.

lists the maximum hardness obtainable at the various reheating temperatures, the time corresponding to this value, and the time range to obtain 90 per cent of the maximum increase in hardness.

The dependence of the tensile properties on time of treatment at 500° C. was determined for a steel containing 1.02 per cent copper and

0.267 per cent carbon. The results, plotted in Fig. 21, show the yield point and tensile strength curves to parallel the hardness curves, while the elongation and reduction of area decrease as the tensile strength increases and vice versa.

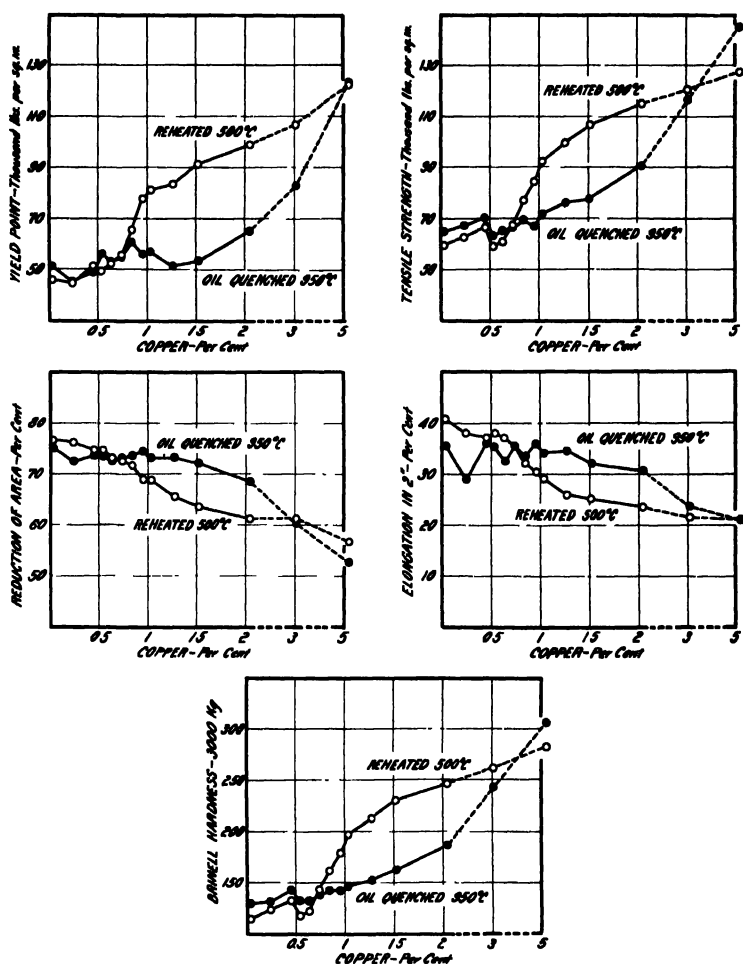


FIG. 15.—INFLUENCE OF COPPER CONTENT ON MECHANICAL PROPERTIES OF 0.03 TO 0.08 PER CENT CARBON STEELS, QUENCHED IN OIL FROM 950° C. AND REHEATED 4 HR. AT 500° C.

The tensile properties of two alloys, containing 1 per cent copper with 0.038 per cent and 0.56 per cent carbon, normalized and reheated for 4 hr. at several temperatures, are shown in Figs. 22 and 23. Both alloys show maximum hardness, tensile strength and yield point and minimum reduction of area and elongation after reheating at 500° C. (930° F.).

At 600° C. (1110° F.) the properties are almost identical with those in the normalized condition.

The previous precipitation treatments have all been made according to the customary practice of cooling the steel from the solution heat

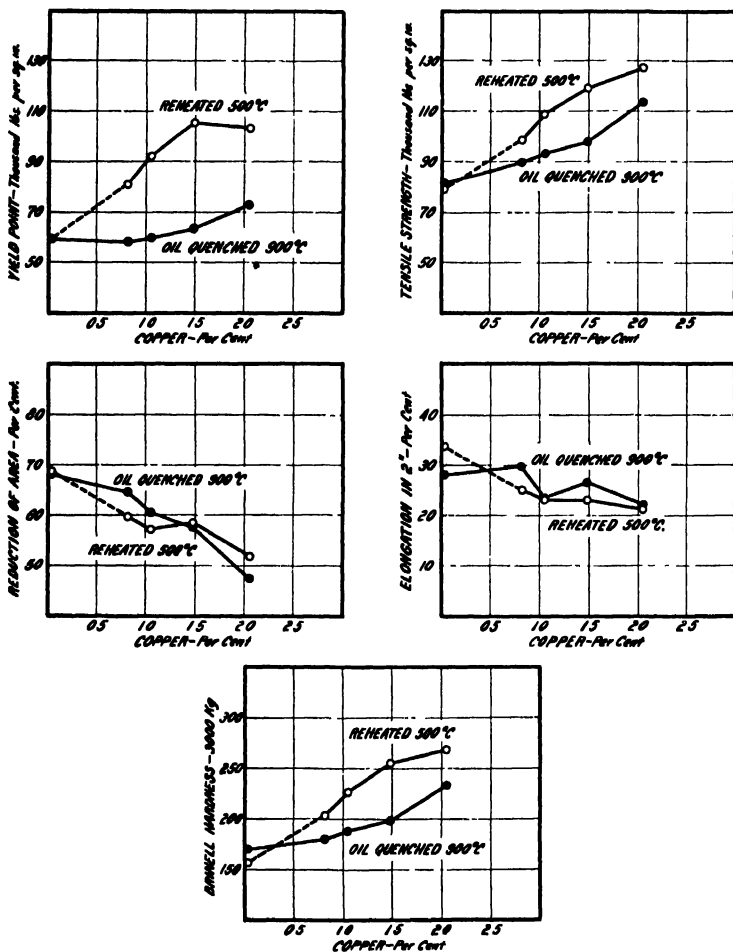


FIG. 16.—INFLUENCE OF COPPER CONTENT ON MECHANICAL PROPERTIES OF 0.20 PER CENT CARBON STEELS, QUENCHED IN OIL FROM 900° C. AND REHEATED 4 HR. AT 500° C.

treatment to room temperature, and then reheating to the temperature of precipitation. An improvement on this consists in cooling the steel directly to the precipitation temperature, without intermediate cooling to room temperature.

In Figs. 24 and 25 are plotted the Brinell hardness values of two copper steels as a function of time of maintaining at temperatures between

450° C. and 600° C. (840° and 1110° F.), for specimens directly cooled from 865° C. (1590° F.) in a salt bath held at the stated temperature. The curves should be compared with Figs. 19 and 20 for the same steels reheated to the same temperatures after air-cooling to room temperature.

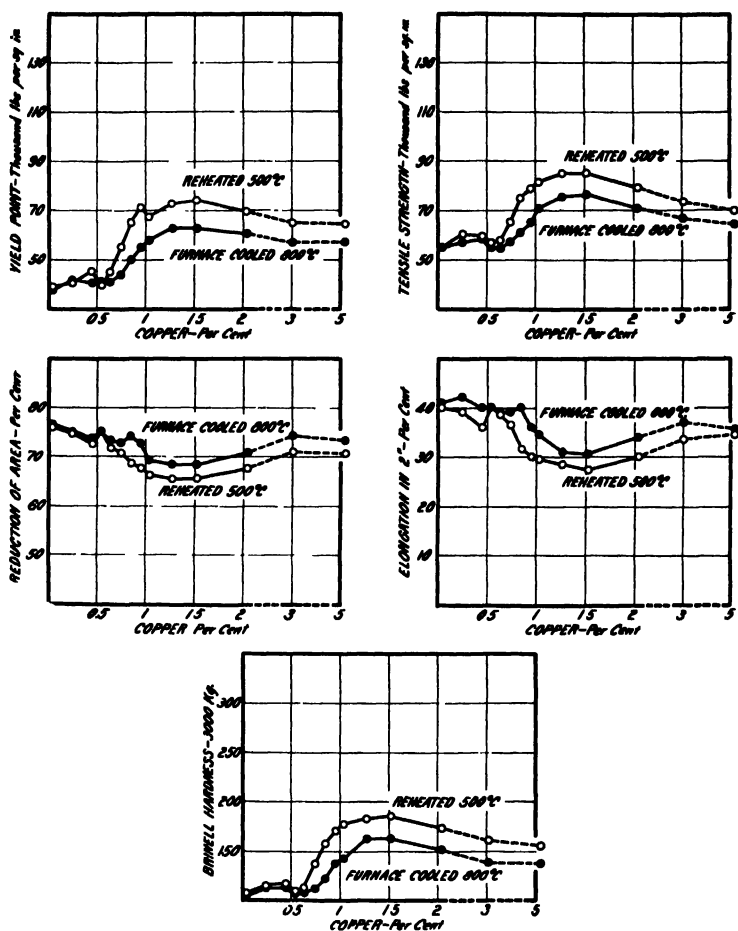


FIG. 17—INFLUENCE OF COPPER CONTENT ON MECHANICAL PROPERTIES OF 0.05 TO 0.08 PER CENT CARBON STEELS.

Furnace-cooled at the rate of 100° C. per hour and reheated 4 hr. at 500° C.

The curves for 450°, 500° and 550° C. (840°, 930° and 1020° F.) are practically identical for the two methods of precipitation treatment. There is, however, a considerable difference between the two time curves at 600° C. (1110° F.) After air-cooling to room temperature and reheating at 600° C. (1110° F.) the alloys harden appreciably in a very short time, and the hardness has fallen off considerably after an hour. On cooling directly and maintaining in the salt bath at this temperature,

the hardening occurs much more gradually (maximum in 2 hr.) and reaches a much lower maximum hardness (169 compared with 197 Brinell for the 0.2 per cent carbon steel).

The explanation of this is concerned with the conditions of nucleus formation under the two conditions of precipitation treatment. On

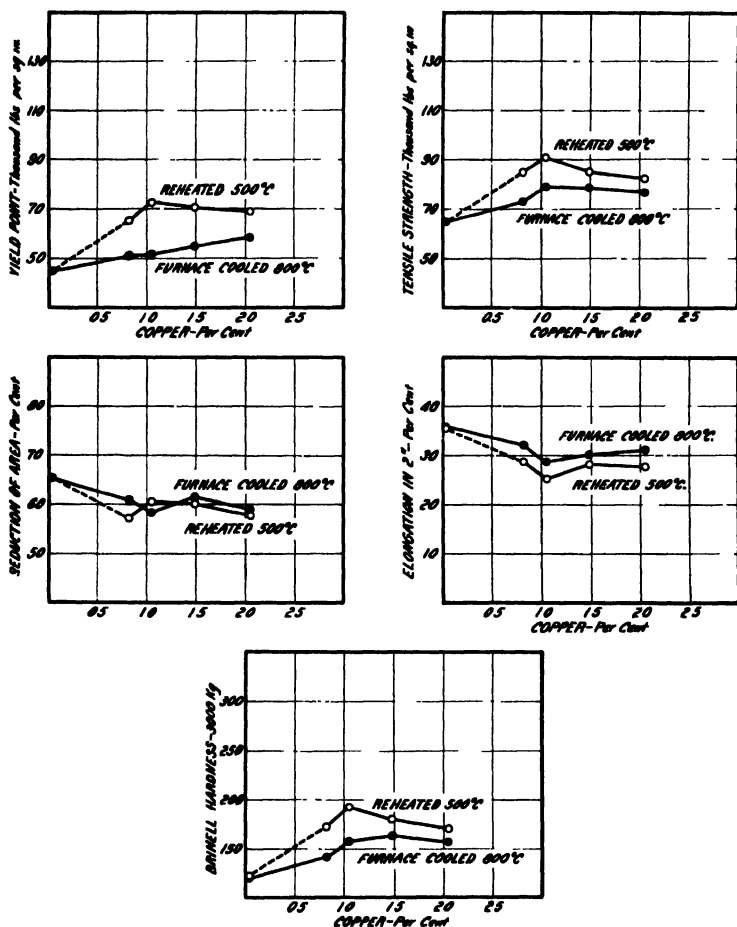


FIG. 18.—INFLUENCE OF COPPER CONTENT ON MECHANICAL PROPERTIES OF 0.20 PER CENT CARBON STEELS.

Furnace-cooled at the rate of 100° C. per hour and reheated 4 hr. at 500° C.

cooling directly to 600° C. (1110° F.) relatively few nuclei form, and, since the rate of diffusion at this temperature is comparatively high, copper will migrate to these nuclei. If the alloy has been cooled to about 550° C. (1020° F.) or below, however, a large number of nuclei are formed very quickly but grow relatively slowly at this temperature; but on reheating to 600° C. (1110° F.) these previously formed nuclei grow

rapidly, resulting in the attainment of maximum hardness in a very short time, followed by a decrease in hardness as the particles exceed the critical dispersion. After a short period of direct treatment at 600° C.

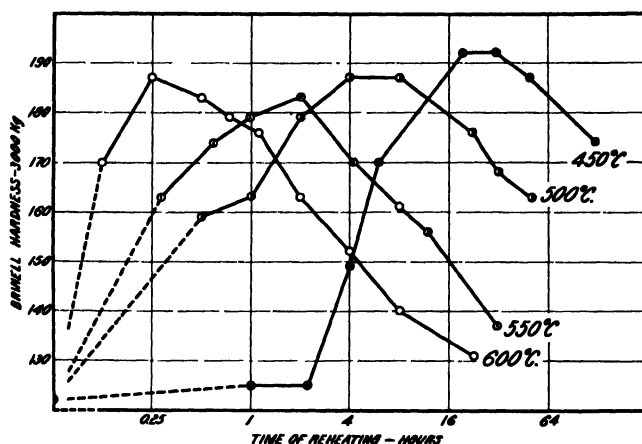


FIG 19—INFLUENCE OF TIME OF REHEATING AT VARIOUS TEMPERATURES ON HARDNESS OF COPPER STEEL

Air-cooled from 865° C. and reheated at temperatures noted. (No. 867: 1.06 per cent copper, 0.061 per cent carbon)

TABLE 4—Time to Reach Maximum Hardness at Various Reheating Temperatures

Reheating Temperature		Time to Reach Maximum Hardness, Hr.	Maximum Hardness, Brinell No	Time Limits to Obtain Over 90 Per Cent of Maximum Increase in Hardness, Hr.
Deg C	Deg F			
ALLOY 867: 1 06 PER CENT Cu, 0 061 PER CENT C				
600	1110	0 25	187	0 2- 0 6
550	1020	2	183	0 9- 2 5
500	930	4	187	2 5-14
450	840	18	192	14 -60
ALLOY 869: 1 07 PER CENT Cu, 0 193 PER CENT C				
600	1110	0 25	197	0 2- 1 0
550	1020	2	197	1 2- 3
500	930	4	207	2 6-10
450	840	32	209	15 -65

(1110° F.) without previously cooling below that temperature, the few nuclei will be so widely scattered that a great part of the copper will still be in solution and only that in the immediate vicinity of the nuclei precipitated. If the alloy in this condition is cooled to lower temperatures and reheated, new nuclei will be formed and precipitation will



occur in the parts removed from the large original nuclei, resulting in an increase of hardness depending on the amount of copper remaining in solution in these areas.

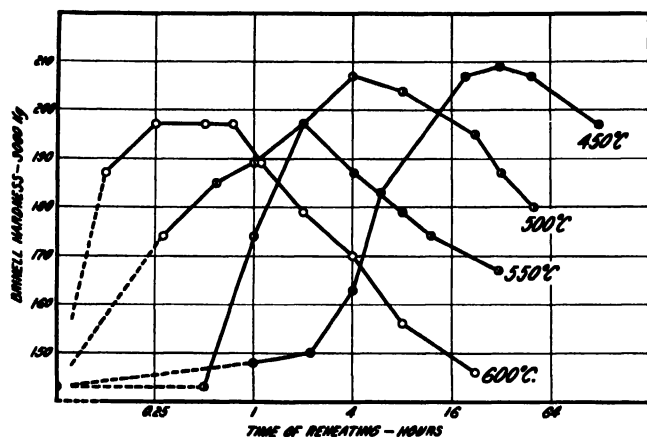


FIG. 20.—SAME AS FIG. 19. (No. 869: 1.07 PER CENT COPPER, 0.193 PER CENT CARBON.)

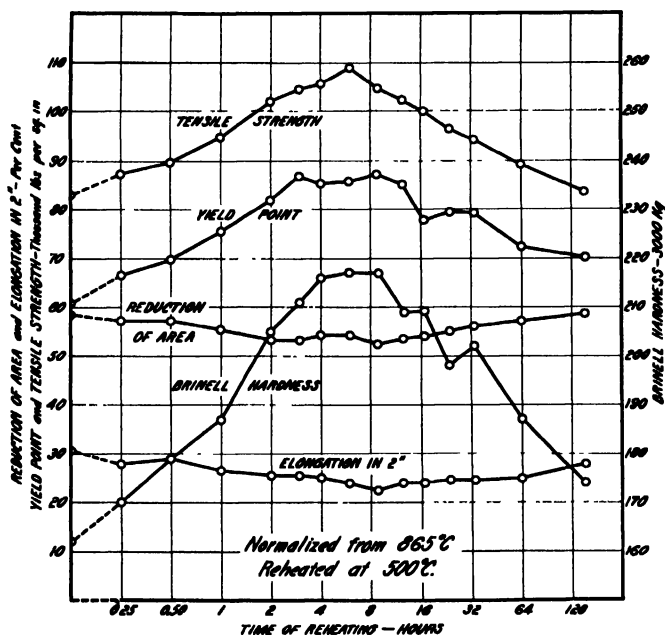


FIG. 21.—INFLUENCE OF TIME OF REHEATING AT 500° C. ON MECHANICAL PROPERTIES OF COPPER STEEL. (No. 939: 1.02 PER CENT COPPER, 0.267 PER CENT CARBON.)

This explanation was substantiated by again reheating at 500° C. (930° F.) the specimens which had previously been given the direct treatment at 600° C. (1110° F.). The resulting Brinell hardness values are

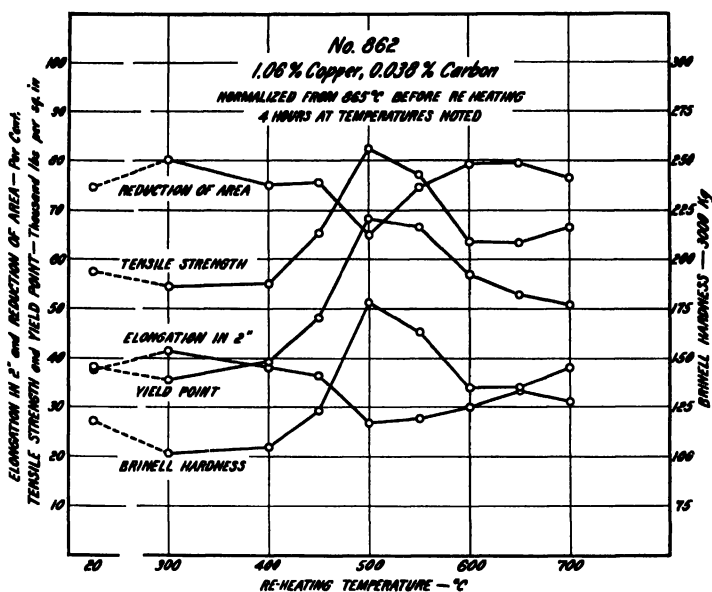


FIG. 22.—INFLUENCE OF REHEATING TEMPERATURE ON MECHANICAL PROPERTIES OF COPPER STEEL. (No. 862: 1.06 PER CENT COPPER, 0.038 PER CENT CARBON.)

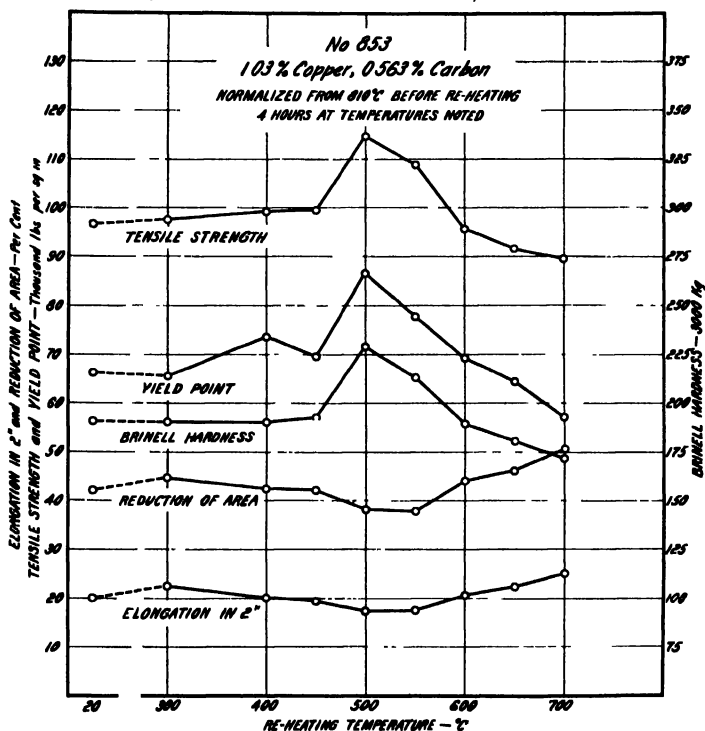


FIG. 23.—SAME AS FIG. 22. (No. 853: 1.03 PER CENT COPPER, 0.563 PER CENT CARBON.)

plotted as dot-and-dashed lines in Figs. 24 and 25, and show a marked, almost maximum, increase in hardness for the specimens held but a short time at 600° C. (1110° F.), but this rapidly becomes less and no further

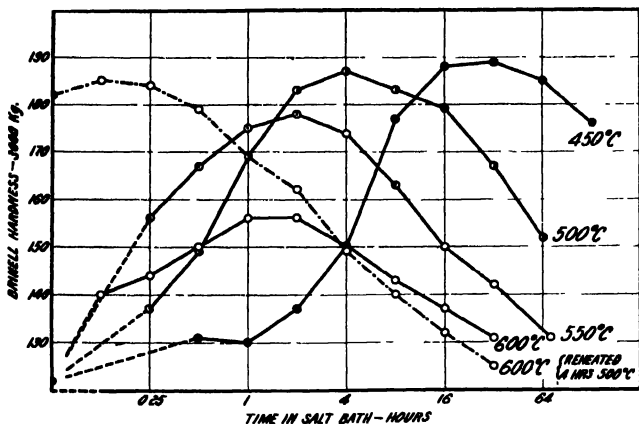


FIG. 24.—INFLUENCE OF TIME AT VARIOUS PRECIPITATION TEMPERATURES ON HARDNESS OF A COPPER STEEL.

Cooled from 865° C. in salt bath maintained at temperatures noted (No. 867: 1.06 per cent copper, 0.061 per cent carbon)

hardening capacity remains after about 4 hr., which was sufficient to throw almost all of the copper out of solution.

Tensile tests confirmed the indications of the hardness measurements that direct precipitation treatment at 500° C. (930° F.) was as effective

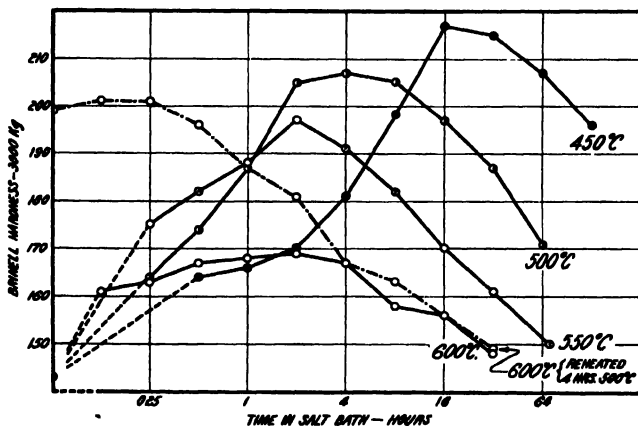


FIG. 25.—SAME AS FIG. 24 (No. 869: 1.07 PER CENT COPPER, 0.193 PER CENT CARBON.)

as reheating to that temperature following air-cooling to room temperature. Table 5 shows the results, which need little comment, save to point out the remarkably high reduction of area figures given by the directly precipitated 0.19 per cent carbon steel. The economies of such a method of treatment, particularly if it follows hot rolling, are obvious.

## IMPACT RESISTANCE OF COPPER STEELS

In Fig. 26 are given curves for the Charpy impact resistance as a function of time of reheating, temperature of reheating, quenching

TABLE 5.—*Tensile Properties of Copper Steels Given Direct Precipitation Treatment Without Intermediate Cooling to Room Temperature*

Heat Treatment	Yield Point, Lb per Sq In	Tensile Strength, Lb per Sq In	Elongation, Per Cent on 2 In.	Reduction of Area, Per Cent	Brinell Hardness
ALLOY 867 1 06 PER CENT CU, 0 061 PER CENT C					
1 Air-cooled to room temperature after 1 hr at 865° C . . . . .	48,400	60,900	38 0	74 4	123
2. Same as 1, then reheated for 4 hr at 500° C . . . . .	73,900	85,800	28 0	67 0	187
3 1 hr at 800° C, cooled in salt bath at 500° C held 4 hr at 500° C . . . . .	71,850	85,100	29 3	67 5	184
4 1 hr at 800° C, air-cooled to 500° C, placed in furnace at 500° C. and held 4 hr . . . . .	70,000	85,100	29 0	67 2	183
5. Same as 4, then held at 500° C, after air cool, for 2 hr . . . . .	68,400	81,900	31 0	67 5	170
6 Same as 4, then held at 500° C, after air cool, for 1 hr . . . . .	64,900	74,900	32 0	69 1	153
ALLOY 869 1 07 PER CENT CU, 0 193 PER CENT C					
1 Air-cooled to room temperature after 1 hr at 865° C . . . . .	51,900	71,600	32 5	60 1	143
2. Same as 1, then reheated for 4 hr at 500° C . . . . .	75,900	95,000	25 0	55 6	207
3. 1 hr at 800° C., cooled in salt bath at 500° C, held 4 hr at 500° C . . . . .	74,150	95,900	26 2	77 3	198
4 1 hr at 800° C, air-cooled to 500° C, placed in furnace at 500° C and held 4 hr . . . . .	74,150	95,600	25 8	77 6	198
5 Same as 4, then held at 500° C, after air cool, for 2 hr . . . . .	72,400	92,600	26 5	78 2	186
6 Same as 4, then held at 500° C, after air cool, for 1 hr . . . . .	64,100	85,200	28 5	75 2	170

temperature, and normalizing temperature, for a steel (No. 895) containing 1.04 per cent copper and 0.080 per cent carbon. The impact specimen was the 10 by 10 by 55-mm. Charpy form with a U-notch 5 mm. deep of radius 1.2 mm. (0.047 in.) at the bottom.

It is evident that the impact resistance is very closely related to the precipitation of the copper. At a precipitation temperature of 550° C. (1020° F.) the steel has recovered an appreciable portion of its initial impact strength, and inasmuch as the tensile strength and hardness have not yet fallen off greatly at this temperature, the use of 550° C. instead of 500° C. suggests itself where impact resistance is a major factor. The same improvement is obtained by increasing the time at 500° C. (930° F.), and evidently corresponds to a supercritical dispersion of the copper.

## COLD-ROLLED COPPER-STEEL SHEET

Fig. 27 shows the yield point, tensile strength and elongation in 2 in. as a function of the reduction of thickness by cold rolling for 0.040-in. sheet of an alloy containing 1.02 per cent copper and 0.023 per cent carbon. The different reductions were obtained by giving the "ready-

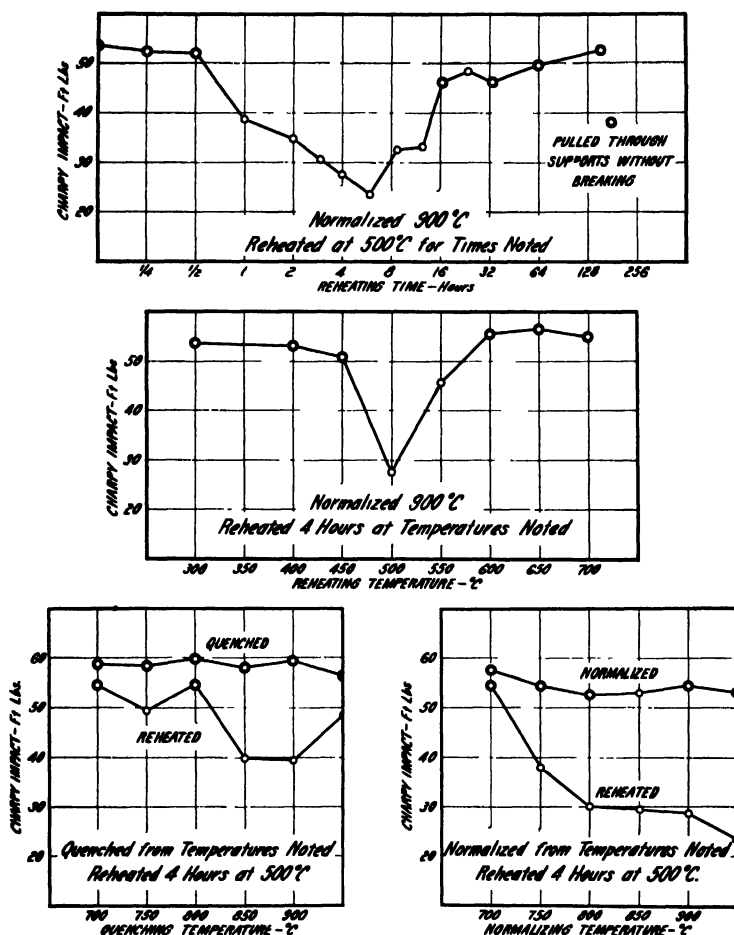


FIG. 26.—EFFECT OF VARIATIONS OF HEAT TREATMENT ON THE CHARPY IMPACT RESISTANCE OF COPPER STEEL. (No. 895: 1.04 PER CENT COPPER, 0.08 PER CENT CARBON.)

to-finish" normalizing treatment at different gages. Table 6 gives further data on the tensile properties.

After reheating, the specimens that received 0 and 10 per cent reduction are found to have hardened appreciably, but with 50 per cent reduction, although the hardness increases, the yield point of the rolled material

is barely maintained, and the strength of the 75 per cent reduction specimen actually decreases except at the lowest temperatures of reheating. Of very great interest is the marked improvement in ductility which occurs without loss of strength when the cold-worked specimens are reheated. This is reflected by an increase of the Erichsen value from 0.304 to 0.330 and from 0.210 to 0.230 in. respectively for the 10 and 50 per cent reduction samples after reheating at 450° C. (840° F.).

### QUATERNARY COPPER STEELS

In Table 7 will be found data on the physical properties of a variety of copper steels containing additions of silicon, manganese, vanadium.

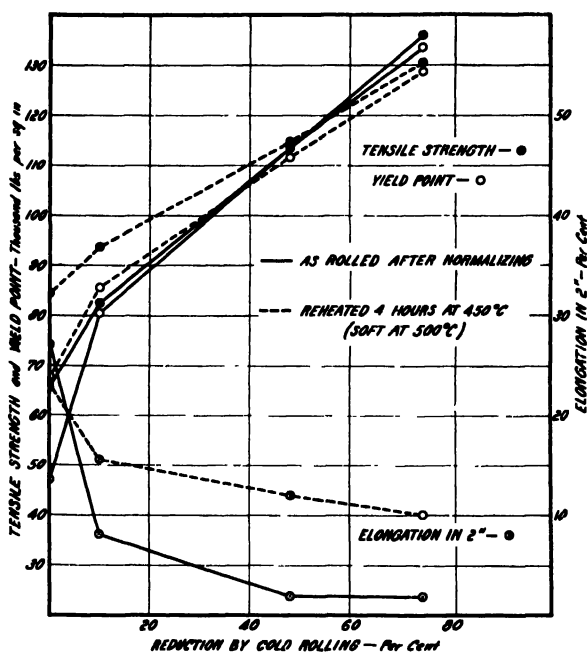


FIG. 27.—INFLUENCE OF REHEATING TEMPERATURE ON MECHANICAL PROPERTIES OF COLD-ROLLED 0.040-IN. COPPER-STEEL SHEET. (No. 896: 1.02 PER CENT COPPER, 0.073 PER CENT CARBON.)

zirconium, chromium, nickel, aluminum, titanium, molybdenum, tungsten, cobalt, phosphorus, and arsenic.

It will be noticed that none of the alloying additions result in a substantial increase of the precipitation-hardening effect, although the base hardness of the alloys varies considerably. The fact that copper precipitation can be applied to almost any type of steel is important, for it is an unsurpassed method of raising the yield point 15,000 to 30,000 lb. per square inch without recourse to difficult quenching treatments.

TABLE 6.—*Properties of 0.040-in. Copper-steel Sheet\**

Alloy 896: 1.02 per cent Cu, 0.073 per cent C, 0.501 per cent Mn, 0.042 per cent Si

Reheating Temperature, Deg C.	Yield Point, Lb. per Sq In 0.5 Per Cent Extension	Tensile Strength, Lb. per Sq In	Elongation, Per Cent on 2 In	Rockwell Hardness	
				B-150	C
NORMALIZED FROM 800° C AND REHEATED 4 HR AT TEMPERATURES NOTED					
Soft	47,000	65,650	27 0	40 0	— 8 7
350	43,050	63,550	26 0	36 2	— 12 8
400	46,700	65,350	27 8	40 4	— 11 0
450	58,200	76,100	23 5	55 0	— 1 8
500	67,850	84,550	23 0	65 4	+ 6 7
550	59,850	75,750	21 0	57 0	+ 2 4
600	56,150	68,200	22 8	49 5	— 4 8
NORMALIZED FROM 800° C, COLD-ROLLED 10 PER CENT REDUCTION AND REHEATED 4 HR AT TEMPERATURES NOTED					
As rolled	80,650	82,650	8 0	66 0	8 8
350	80,650	87,400	11 8	72 3	12 1
400	80,050	88,100	13 0	71 4	11 2
450	85,550	93,800	15 5	74 8	12 9
500	80,700	89,700	17 5	72 8	13 2
550	70,350	80,700	16 8	65 6	7 1
NORMALIZED FROM 800° C, COLD-ROLLED 50 PER CENT REDUCTION AND REHEATED 4 HR AT TEMPERATURES NOTED					
As rolled	113,550	113,550	1 8	83 2	20 8
350	113,200	115,200	8 3	85 5	22 6
400	110,000	114,650	10 5	85 5	23 2
450	111,500	114,800	12 0	86 6	23 6
500	102,700	107,100	12 8	83 2	21 2
550	92,550	96,950	12 8	78 8	16 7
NORMALIZED FROM 800° C, COLD-ROLLED 75 PER CENT REDUCTION AND REHEATED 4 HR AT TEMPERATURES NOTED					
As rolled	113,500	135,900	1 8	89 2	25 5
350	135,800	137,050	3 3	92 4	28 6
400	130,050	134,050	6 0	91 4	28 2
450	128,650	130,300	10 0	91 2	27 7
500	118,550	118,750	11 5	86 6	24 4
550	106,700	107,150	11 5	83 0	20 0

\* All material tested at 0.040-in. gage. The different reductions were obtained by giving the 800° C. normalizing treatment at 0.040, 0.044, 0.077 and 0.156 in. thickness

## MICROSTRUCTURE

Inasmuch as the high-temperature heat treatment of copper steels retains the copper content (up to about 1.5 per cent) in solid solution, and the subsequent low-temperature treatment causes a precipitation of copper which is submicroscopic, the microstructures of the 1 per cent copper steels are essentially the same as copper-free steels of otherwise

identical composition and heat treatment. A visible copper precipitation is obtained by annealing for long times at temperatures above 650° C. The copper appears as very small slightly elongated particles with no obvious tendency to form a Widmanstätten figure. Clearly visible precipitates were obtained in alloys that contained sufficient silicon to render alpha stable at high temperatures.

#### SUMMARY AND CONCLUSIONS

The influence of variations in heat treatment and composition on the mechanical properties of copper steels has been studied. Steels containing more than 0.7 per cent copper are capable of being hardened by precipitation, and possess the best properties after normalizing (air-cooling) from temperatures in the neighborhood of 800° C. (1470° F.) and reheating to cause precipitation of the copper retained in metastable solution by the normalizing treatment. Unlike most precipitation-hardening alloys, quenching or other rapid cooling following the solution heat treatment is not necessary. A free air cooling even of comparatively heavy sections is sufficient to give almost maximum properties after reheating. Some precipitation-hardening occurs during the cooling operation if the rate is less than 25° C. (45° F.) per minute, but the final properties after reheating are not affected until the rate is less than 1.5° C. (3° F.) per minute (100° C., 180° F., per hour). The precipitation treatment may be applied directly to hot-rolled or forged shapes without special normalizing treatment. The simplicity of the precipitation treatment and the fact that quenching, with its attendant danger of warping or cracking, is not necessary should render the steels very useful in many applications where a cheap medium-strength steel is required without expensive heat treatment, or where complicated sections are concerned.

Curves are given showing the interdependence of time and temperature for the reheating treatment. Maximum hardness is obtained in 24 hr. at 450° C., 4 hr. at 500° C. and 15 min. at 600° C.; with longer times the steel softens again. Equally good results can be obtained if the steels are air-cooled from the high-temperature solution heat treatment to about 500° C. and maintained there for the precipitation treatment without intermediate cooling to room temperatures.

Precipitation-hardening first appears with about 0.7 per cent copper and reaches a maximum with 1.5 per cent copper, beyond which no advantage is gained, except in the quenched condition. Precipitation-hardening is additive to the base hardness of carbon steels, although the increase due to precipitation becomes rather less as the carbon content is increased.

As an example of typical properties, a steel containing 1.45 per cent copper, 0.202 per cent carbon, had a yield point in the normalized condi-





977	1.0	.185	.091(Zr)	845	53500	74800	35.3	65.5	81750	93750	27.0	59.1	147	-	156	197	186
978	1.0	.106	1.13(Gr)	900	52300	67150	25.5	75.3	79480	88000	30.5	71.6	154	-	140	197	175
979	1.0	.256	1.14(Gr)	900	69600	89900	35.5	67.4	90900	108900	26.0	64.0	175	-	168	222	207
<hr/>																	
980	1.0	.092	$\frac{M}{1}$		53380	67100	31.5	60.8	61900	93500	27.5	65.7	166	-	190	198	185
981	0.998	.077	2.61	845	55000	77500	33.0	64.8	80650	98700	28.0	64.0	154	-	170	196	179
982	2.01	.086	2.58	845	74600	105800	24.0	54.6	103800	108800	26.0	59.8	203	217	231	226	196
983	1.0	.215	3.51	845	43000	102200	24.5	46.1	93500	103750	24.8	56.8	196	-	213	219	202
984	1.0	.215	2.54	845	68800	92800	28.5	57.0	90450	104750	25.3	57.1	190	-	204	217	197
986	1.0	.201	1.01	845	65100	94150	35.0	59.4	96050	109400	26.0	55.5	163	-	180	206	196
<hr/>																	
1007	1.0	.189	.980(Al)	845	61500	77500	35.8	64.1	77250	94980	24.5	59.6	149	-	163	191	182
1008	1.0	.176	.934(Fe)	845	64850	78000	32.8	74.6	89350	96900	23.8	65.5	156	-	163	190	179
1009	1.0	.243	.963(Mn)	900	65450	121580	19.0	50.9	108300	134080	20.3	55.6	245	-	227	233	206
1010	1.0	.227	.980(W)	900	80400	89480	26.5	56.1	99700	106850	25.0	55.5	199	-	188	217	207
1011	1.0	.215	3.56(Cu)	845	63800	86000	30.8	62.8	89600	105400	25.8	57.4	165	-	172	216	197
1012	1.0	.208	1.00(Co)	845	63000	80000	32.0	63.3	84050	100050	25.5	56.8	154	-	166	204	197
<hr/>																	
1164	1.25	.257	$\frac{P}{210}$	900	75400	99500	25.0	44.9	99700	117700	21.5	46.9	189	194	228	229	216
1165	0.68*	.08*	.11*	900	84000	71600	34.0	66.9	68600	76900	25.0	64.9	138	137	145	162	149
1166	1.07	.050	.165	900	59500	69000	29.0	74.9	84700	92400	27.5	66.2	136	137	179	195	179
1167	2.12	.046	.328	900	58300	96100	25.0	64.3	101500	108400	26.0	64.1	212	218	246	241	211
<hr/>																	
1169	1.0*	.08*	$\frac{S_1}{.50^*}$										161	166	196	186	170
<hr/>																	
1170	1.0*	.08*	$\frac{S_2}{.50^*}$										145	145	170	179	186
<hr/>																	
1171	1.0*	.065	$\frac{M}{.507}$	900	59300	71600	35.0	66.2	79300	93500	25.5	65.1	156	145	163	196	186

All steels forged perfectly except those containing tin and antimony, which were forgeable only with extreme care.

q = Silicon steels were quenched from temperatures stated.  
 z = Reannealed at 450° C. for 4 hours  
 \* = Intended composition, not analyzed

tion of 69,600 lb. per square inch, tensile strength 85,200 lb. per square inch, elongation 29.5 per cent, reduction of area 60.1 per cent, and Brinell hardness 170. Reheating for 4 hr. at 500° C. increased the yield point and tensile strength to 90,000 and 107,800 lb. per square inch respectively, while the elongation and reduction of area dropped to 23.5 and 54.8 per cent, the Brinell hardness being 223. These results were obtained on laboratory melts and commercial heats would undoubtedly be superior.

Several special steels containing copper with additions of the common alloying elements were made. Although in no case was the actual increase due to precipitation modified greatly, the higher base hardness resulted in some excellent properties after normalizing and reheating.

#### ACKNOWLEDGMENTS

This work was done in the Copper Alloys Research Laboratory of The American Brass Co., at the request of the Anaconda Copper Mining Co. The authors express their gratitude to both companies for permission to publish the results. Mr. W. H. Bassett, Metallurgical Manager of The American Brass Co., has had general supervision over the work, and without his guidance and encouragement it could not have been completed. Analyses were performed in the chemical laboratory of The American Brass Co., mainly by Mr. C. H. Osborne, and the mechanical tests—themselves a formidable part of the work—were done under the direction of Mr. C. F. Schmid. To these gentlemen, and to all others in The American Brass Co. who have been of assistance, the authors wish to express their sincere thanks.

#### DISCUSSION

*(H. Foster Bain presiding)*

F N. SPELLER, Pittsburgh, Pa.—Will someone give us some definite information on the value of copper steel with or without heat treatment? Ten years ago or more we started to investigate the effect of copper, and for several years made 1 per cent copper steel, but so far have not had the success with hot-rolling this steel that the author predicts. That is to say, the surface finish is somewhat inferior to plain carbon steel.

What are the real advantages of high-copper steel, aside from added resistance to corrosion we get under atmospheric and other rather limited conditions? What advantage is there in getting the physical properties reported by the author by precipitation, other-than by raising the carbon slightly?

In meeting certain specifications of the Petroleum Institute, for instance, using tubing with 1 per cent copper steel, we lower the carbon proportionately and apparently get as good physical properties as with higher carbon without copper.

Regarding corrosion resistance, which is the outstanding objective in some cases, much remains to be learned. There is no question about the advantage of copper steel under atmospheric conditions. We found in our early studies of high-copper steel that apparently it gave unusually good resistance in certain kinds of saline

waters, but in others it was no better than carbon steel. So, for that reason, we have hesitated to push this material commercially because of the danger of not being able to predict where it will pay to use it in service.

H. W. GILLETT, Columbus, Ohio.—I can answer one of the questions in regard to fatigue. In the nonferrous alloys we often have the situation where we get tensile strength by precipitation-hardening but do not get a corresponding increase in endurance. That is true in some aluminum alloys and quite a few copper alloys. But these precipitation-hardened copper steels have the same ratio of tensile strength to endurance limit when the strength is obtained in this way as when it is obtained by heat treatment or by alloying.

It seems to me Dr. Speller is talking about a particular case where he has to meet a specification that he can meet, as far as tensile strength goes, in a number of ways. His product is probably good enough from that point of view without the additional strength due to copper, but there are many other applications where it is desirable to gain either a little added strength or to gain that strength without loss in toughness. That is where the addition of copper and the use of precipitation-hardening are outstanding.

It is remarkable that no matter what is done with copper steel in the way of adding other alloys, the effect of the copper shows up when the precipitation-hardening treatment is applied. It moves the yield and tensile up about 20,000 lb. without normally depreciating the toughness at all. In fact, in my own mind, I think of this class of steels as the "plus twenty" class. You can gain about that much by the simple precipitation-hardening operation.

A. V. DE FOREST, New York, N. Y.—There are a few applications of precipitation-hardening that might be interesting. I would like to hear Dr. Gillett remark on the nonelastic behavior of ordinary materials as compared with the precipitation-hardened materials.

I have had to do with improving the elastic properties of metals in the attempt to make a perfect spring for weighing purposes into which fatigue properties do not enter, but departures from Hook's law are extremely important. Starting in with hysteresis figures derived from Foppl's work, in which he shows that precipitation-hardened dural is the most elastic material that he has tested, we tested a few other precipitation-hardened systems particularly prepared by quenching, cold working, and then precipitation-hardening.

We found we could add very greatly to the elastic behavior of almost any of the normal cold-workable materials by proper cold work and proper reheating. We decreased by 90 per cent the amount of creep in 24 hr., and the amount of direct hysteresis on loading and unloading by so doing.

On the other side of that question come the fatigue properties. If we increase radically the elastic behavior, we decrease the hysteresis absorption possibilities of the material, and according to Foppl's ideas of hysteresis, we may seriously interfere with the fatigue resistance of the metal in the presence of small notch effects. I should like to hear more as to that.

H. W. GILLETT.—We have no indication that these steels are particularly susceptible to notch effects. We have no data on the damping properties and I am afraid at the present time very few of us aside from de Forest and Von Heydecampf have much of an idea of what damping properties mean when we get them.

C. H. LORIG, Columbus, Ohio.—We have made a study of the rolling characteristics of copper steels for the Copper and Brass Research Association. Our results showed that when high-copper steels are heated in an oxidizing atmosphere a film of copper is formed beneath the oxide, and that, if this steel is forged or rolled at a temperature much above 2000° F., this copper diffuses into the steel and causes checking of the surface. We found, further, that this phenomenon can be prevented

by rolling at a temperature of 2000° F. or lower, by heating in a nonscaling atmosphere, or by alloying nickel with the steel.

Our laboratory tests demonstrated the effectiveness of nickel in eliminating checking and these results were confirmed in mill practice on seamless steel tubes pierced and rolled from high-copper steel billets to which nickel, in small quantities, was added.

The laboratory tests were made on small upright cylindrical specimens that were heated to a given temperature for a given time, then forged into disks with an air hammer. The unsupported rim of the disks is a highly sensitive indicator of the characteristic surface checking occurring on hot-working plain high-copper steels. It is even more sensitive and more drastic in its effect than the action of rolls in rolling-mill practice where the surfaces of the steel sections are supported by the rolls.

In one plant test, several billets of 1 10 per cent copper steel containing various amounts of nickel were pierced and rolled into seamless tubes. The billets were pierced at such a temperature that, at the outcoming end of the piercing machine, they were at 2235° F. The tubes were then finished hot-rolled at 3-in. outside diameter. Inspection showed them to have excellent surfaces free from the characteristic checking shown by high-copper nickel-free steel. A nickel content of 0.25 per cent was sufficient to prevent the surface checking.

In our laboratory forging tests, most of the usual alloying elements were added to copper steels to determine their effects on the hot-working characteristics of the steel. The upper limit of these elements were: nickel, 2.5 per cent; manganese, 2; vanadium, 0.23; cobalt, 3.50; zirconium, 0.20; chromium, 1.15; aluminum, 1.1; titanium, 1.0; molybdenum, 1; tungsten, 1; tin, 0.25; phosphorus, 0.13; and silicon, 0.35 per cent.

The only other element besides nickel that had an important effect on the surface appearance of copper steels forged above 2000° F was cobalt. Molybdenum appeared to be slightly beneficial, but all other elements were without effect. The claims that both chromium and manganese are beneficial could not be verified.

In the tests with nickel, carbon was varied from 0.20 to 1.00 per cent and copper from 0.20 to 4.0 per cent. The temperature at which the samples were forged was varied from 1400° to 2350° F. Surface fissures were not detected until temperatures above 2000° F. had been reached. The depth of these fissures increased with the temperature. The depth of fissures also increased with copper contents and also slightly with carbon contents. Below 0.70 per cent copper they were shallow and unimportant. In most cases the amount of nickel required to prevent the surface checking increased with the copper content.

The nature of the surface checking prevalent in some hot-worked plain copper steels is not, in reality, a case of hot-shortness, but is instead a surface phenomenon completely divorced from the action of the interior of the metal. It is seemingly caused by the copper film which forms beneath the scale of copper steels heated in oxidizing atmospheres.

So far as we know, the first investigators to suggest a correlation between this copper film and the rolling characteristics of the steel were Shunkyo Kodama and Isamu Kotaira, who published their individual researches in the *Journal of Ferrous Metals* (Japan), vol. 8, 1928. In his tests Kodama showed a rapid diffusibility of copper in solid iron at temperatures above 1100° C. (2012° F.). The copper, entering into the boundary of the ferrite crystals, destroys the adhesion between surface grains to such an extent that in subsequent hot-working they no longer remain integrally bonded but separate to form surface fissures. He then concluded, and we have confirmed his results, that in the surface oxidation of steel the unoxidized copper enters the boundary of the ferrite grains and that this constitutes the primary cause for fissures during hot rolling.

We found that the copper film would not interfere with the working of the steel at any temperature below 2000° F. Also, if the steel is heated in a nonscaling atmosphere, such as pure nitrogen, hot-working temperatures above 2000° F. are permissible without danger of surface checking. However, if a plain carbon steel is sprayed with a thin copper film before heating in nitrogen, it is just as susceptible to surface checking at working temperatures above 2000° F. as the copper steels heated in an oxidizing atmosphere. This evidence is ample to demonstrate that it is the copper film that is the primary cause for surface fissures.

The mechanism by which nickel functions to suppress the action of the copper film is not clearly understood. Perhaps the diffusibility of the copper in the iron is altered in the presence of nickel, or perhaps the character of the scale formed on the steel is changed. Our tests suggest that it might even be directly related to the effect of nickel on raising the solidus temperature of the copper-nickel alloys. We do know, however, that small percentages of nickel will prevent the film from penetrating the boundaries of the surface crystals, thereby offsetting any tendency for the high-copper steels to surface crack upon hot working.

Copper steels are then no more hot-short than carbon steels. As a matter of fact, the evidence on hand indicates that the higher sulfur steels containing copper are less hot-short than are those free from substantial amounts of copper. There is considerable controversial discussion in the literature as to the occurrence or non-occurrence of hot-shortness in copper-bearing steels. Some of the most unusual statements are made regarding the effects of such elements as sulfur, manganese, and chromium, and until the Japanese investigators clarified the question by presenting their theory of surface penetration of molten copper the opinions on hot-shortness in copper steels were very conflicting.

To prohibit the surface checking during the hot working of copper steels there are now several means available. If desired, the steels may be hot-worked below 2000° F. without the appearance of fissures, but, as this temperature is often below the usual hot-working temperatures, the method is applicable only to restricted cases; or they may be heated before hot working in a nonscaling atmosphere, which method for the time being, at least, is seemingly impractical; or they may be alloyed with small quantities of nickel, the method we found to give the greatest assurance for successfully working the high-copper steels at high temperatures.

F. N. SPELLER—Confirming Dr Lorig's remarks, there is no question in our mind that copper steels are not red-short. We have rolled a considerable tonnage of copper steel in the last 10 years. The surface checking referred to is extremely light.

We have just tested out the effect of nickel on samples of copper steel furnished from the Battelle Institute and got better results with respect to surface finish. It seems doubtful whether as good results could be obtained by control of temperature. In piercing hot billets for seamless tubing, there is a limit on the temperature range, so perhaps on that account we have been unable to overcome the tending to scamy surface by modifying the working temperature. It will be very satisfactory if there should be developed another solution of the problem at a reasonable cost.

MEMBER—Has silicon any effect—silicon content around 1 per cent?

MEMBER—Is there any danger that copper may form eutectics that would be fluid at reduced temperature; that would tend to cause hot cracks in steel during freezing due to copper, of course?

F. N. SPELLER.—We have experimented up to 1.5 per cent copper and found no separation at all under 0.9. I do not think we have entirely exhausted that subject. We endeavor to keep the steels under 1 per cent and then feel pretty safe, as far as the body of the metal is concerned, but we still have this very fine fish-scale scamy surface, whatever you want to call it. It is not really an objection as far as the usefulness

of the steel is concerned, but it raises the question in the minds of users sometimes, and we would just as soon not have it.

**MEMBER.**—Has any consideration been given to the possible use of these steels at higher temperatures; as to whether these increased properties from precipitation-hardening can be maintained at higher temperatures and might make rather useful material for a temperature service somewhat lower than the temperature at which the higher casts were developed?

**H. W. GILLETT.**—There is considerable evidence that a little copper, perhaps more than is required for ordinary precipitation-hardening purposes, does help high-temperature properties, and it would look to me as though perhaps 0.5 per cent molybdenum and 1.5 per cent copper should make pretty good material for moderately high temperature service. There are some short-time high-temperature data on this subject, but I know of no actual creep tests. The subject would be well worth study.

**C. S. SMITH** (written discussion) —Most of the points raised in the discussion were answered by the remarks of Dr. Gillett or Dr. Lorig, or will be found in the printed paper, which was not available at the time the work was presented for discussion. The remarks of Dr. Lorig on the nature and prevention of surface cracking of copper steels when worked above the melting point of copper are particularly valuable, and it is interesting to see that commercial confirmation of his experiments has been obtained by Dr. Speller. So many conflicting statements have appeared in the literature regarding the influence of copper, but now that the reasons for the surface cracking are definitely known it can be easily overcome.

## Oxide Analysis by Iodine Extraction in Steelmaking Problems

By J. J. EGAN,\* W. CRAFTS\* and A. B. KINZEL,† New York, N. Y.

(New York Meeting, February, 1933)

ADVANCES in the production of quality steel have emphasized the need for greater knowledge of the amount and distribution of oxygen in the steel. Control of inclusion content and quality is largely dependent on such knowledge. While many analytical methods have been devised for the accomplishment of this end, few are without serious limitations in accuracy, convenience, or skill required in application. Usually at least two methods are necessary to determine total oxygen and constituent oxides.

Because of the great importance of this problem and the specific interest in the application of such methods of analysis, the various procedures were carefully reviewed at the Union Carbide and Carbon Research Laboratories, with the view of developing a method free from the limitations mentioned above. Intensive experimentation finally led to an improved iodine extraction analysis described by Cunningham and Price.<sup>1</sup> After this had been thoroughly checked from the standpoint of the analytical chemist, it was rechecked from that of the metallurgist. This involved preparation of a number of small heats of varying composition with determination of total oxygen in the molten metal by the alumina method<sup>2</sup> and an analysis of the solidified material without the aluminum addition by means of iodine extraction; the oxides of iron, manganese, silicon and aluminum also being determined by the iodine analysis. The report of this work constitutes the subject of this paper.

### THE IODINE METHOD

Fundamentally the iodine method is well established. It is based on the procedure first described by Eggertz,<sup>3</sup> and depends upon the fact that iron, manganese, silicon and aluminum, as well as the metallic constituents of the pertinent sulfides, carbides and nitrides of these metals

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<sup>1</sup> T. R. Cunningham and J. R. Price: *Ind. & Eng. Chem., Anal. Ed.* (1933) **5**, 1.

<sup>2</sup> C. H. Herty, Jr., H. Freeman and M. W. Lightner: *U. S. Bur. Mines Rept. of Investigations* 3166 (1932).

<sup>3</sup> V. Eggertz: *Polytechnisches Jnl.* (1868) **168**, 119.



are soluble in a solution of ferrous iodide. The oxides are insoluble and remain in the sludge, which is filtered off and analyzed by standard methods for the elements mentioned, the results being calculated back to the oxides. The method is limited, however, to plain carbon or manganese steels. It does not apply to steels containing the stable carbide-forming elements such as chromium, vanadium or tungsten; the carbides of these elements are not decomposed in the iodide solution, and remain in the residue, therefore the analysis of the latter does not indicate the oxidic content of such steel with sufficient accuracy.

The sulfides of manganese and iron are decomposed by the iodine solution. The sulfur is precipitated quantitatively, and the manganese and iron are dissolved. That this reaction is quantitative in character has been checked repeatedly; for example, a low-carbon steel containing 0.021 per cent sulfur was dissolved by the iodine solution, and the residue showed an identical sulfur content. The carbides of iron and manganese are similarly decomposed.

The alumina method was used as a check on the total oxygen as obtained by iodine extraction. While the absolute accuracy of the former method has not been quantitatively proved, there is little room for doubt that the addition of an excess of aluminum to the molten steel converts practically all the oxygen present into alumina. Analyses by the iodine method of steels so treated showed complete absence of  $\text{FeO}$ , with only traces of  $\text{MnO}$  and  $\text{SiO}_2$ . These results, as well as those described in the present work, indicate that both methods account very successfully for the total oxygen present.

#### EXPERIMENTAL PROCEDURE

In order to obtain material on which comparative analyses for total oxygen by the alumina and iodine methods might be made, split heats were used. One-half of each heat was rapidly cooled and used for iodine extraction. The other half was killed with an excess of aluminum, poured into a small mold, sampled, and analyzed for alumina. Considerable difficulty was encountered at first in bringing about sufficiently rapid cooling of the sample for iodine analysis. Molds of many types and sizes failed to produce sound metal in the unkilld heats. Even small water-cooled copper molds were not satisfactory. The desired result was finally obtained by pouring the metal into iced brine, the resulting shot being then carefully selected and sand-blasted before analysis.

The heats made are listed in Table 1. They were chosen to represent wide variation in oxygen content as well as ranges of composition comparable to those of commercial carbon steels. They may be divided broadly into two classes: the unkilld and the silicon-killd. In each group low and high carbon as well as low and high manganese are present, with some variations in the silicon as well. Two heats of high sulfur

TABLE 1.—*Experimental Heats*

Heat No.	Analysis, Per Cent							
	C	Mn	Si	SiO <sub>2</sub>	MnO	FeO	Total O <sub>2</sub> Iodine	Total O <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>
1	0 03	0.02	0 003	0.004	0 013	0 747	0 171	0 177
1A	0 02	0.03	0 001	0 002	0 026	0.826	0 192	0.189
2 <sup>a</sup>	0 03	0 03	0 002	0 002	0.015	1.100	0 260	0.242
3 <sup>b</sup>	0 03	0 27	0 002	0.002	0 170	0 523	0 155	0 140
4	0 03	1.24	0 002	0.002	0.046	0.250	0.067	0 070
5	0 91	0 53	0 004	0.002	0.004	0.180	0 042	0.050
6A	0 76	1 59	0 003	0 002	0 005	0 097	0 023	0 029
6B	0 86	1 51	0.005	0 002	0 004	0 103	0 025	0 031
6C	0 85	1 63	0 006	0 004	0 005	0.111	0.028	0 031
7	0 03	0 43	0 021	0 030	0 065	0 115	0 057	0.062
8	0 03	0 45	0 57	0 097	0 004	0.030	0 060	0 059
9	0 03	1 50	0 26	0 044	0 004	0 048	0 035	0.038
10	0 56	0 61	0.25	0 046	0 004	0.026	0.032	0.036
11	0 93	0 54	0 28	0 050	0 004	0 040	0 037	0 038
12	0 82	0 51	0 85	0 050	0 002	0 024	0 032	0 032
13	0 94	1 65	0 35	0 042	0 003	0 010	0 025	0 028
14	0 94	1 52	0 72	0 060	0 005	0 040	0 042	0 039

<sup>a</sup> Sulfur, iodine sample, 0.790 per cent; aluminum sample, 0.560 per cent.

<sup>b</sup> Sulfur, iodine sample, 0.152 per cent; aluminum sample, 0.134 per cent.

content are shown, which were made in order that the possible effect of this element might be studied.

The heats were made in the high-frequency furnace, in a magnesite-lined crucible, using ingot iron as a base. In the low-carbon heats, iron oxide (Fe<sub>2</sub>O<sub>3</sub>) was added immediately upon melting to insure a constant iron oxide content at the start. Alloy additions were made with manganese and silicon metal, and carbon additions with lumps of graphite. One-half of each heat was poured into the iced brine solution and aluminum was added to the second half in the form of ¼-in. rod of high purity, in amount equal to about 1.5 per cent. The operations from the first pouring into the brine to the final pouring of the aluminum-killed metal were carried out with the utmost expedition, and required less than one minute for completion. Accordingly, there was very little time for change in total oxygen content.

In the choice of material for the iodine analysis only the smaller "shot" was chosen, as this was always the soundest, the larger lumps having cooled somewhat more slowly, with increased possibility of blowholes. The metal was carefully sand-blasted and examined under the binocular

microscope for possible holes, or particles of oxide or adhering sand, and washed with absolute alcohol before analysis. Samples from the aluminum-killed ingots were prepared by drilling through the ingot at the top, center and bottom. Here again, all precautions were taken to prevent oxidized portions about the pipe from entering the sample, as well as to prevent the ingot from heating up excessively during the drilling. The drillings were then well mixed and a representative sample taken for alumina analysis, which followed the usual procedure. Details of the iodine method are appended for convenience.

### DISCUSSION OF THE METHOD

Even a casual examination of the comparative results of the two methods for total oxygen, which are shown graphically in Fig. 1, reveals the excellent checks obtained. The results are particularly satisfying in view of the very radical difference in the two analytical procedures. These figures show definitely that the iodine method is accounting for all of the oxidic content given by the alumina method and it may also be considered that this constitutes a check of the absolute values obtained by the alumina method. Thus, we may conclude that the iodine method gives an accurate total oxygen value.

It is interesting to consider the minor deviations in the total oxygen content obtained by the two methods in connection with a few of the heats shown in the graph. Heats 5, 6A, B and C give low iodine values. This is to be expected because of the inability to get absolutely sound metal in the shot with the high-carbon, high-manganese unkilld steel. The

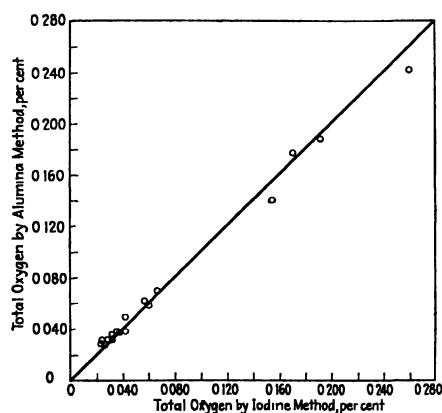


FIG. 1.—COMPARISON OF TOTAL OXYGEN OBTAINED BY THE IODINE AND ALUMINA METHODS.

high-sulfur heats 2 and 3 require special consideration, as the oxygen content shown by the iodine method is higher than that shown by the alumina method by an amount that is greater than the normal error. However, analysis of the aluminum-killed portion of the heat by the iodine method gave a total oxygen value identical with that obtained by acid extraction. Further work showed that the aluminum-killed portion of the sample contained less sulfur than the unkilld portion, indicating that both sulfur and oxygen have been eliminated

from the aluminum-killed portion of the steel, thus accounting for the apparent discrepancy in the analyses made by the two methods in question.

The data above show that the iodine method gives satisfactory total oxygen by means of the sum of the various constituent oxides. It should be noted not only that the method is accurate but that it is extremely practical from the standpoint of the steelmaker and user. No unusual analytical technique and no special apparatus are required. The time necessary for analysis is reasonable, the solution of the average sample being accomplished in approximately three hours, practically no attention being required during this period. The analysis of the residue is common to most extraction methods and takes about two hours.

#### DISTRIBUTION OF CONSTITUENT OXIDES

In the analysis of the constituent oxides, which indicate the type of inclusions present, the iodine method is believed to have a wide field of application. No method has been devised of positively proving that the distribution as shown by the iodine method is accurate, but the fact that the sum of the constituents gives a total check and that the FeO, MnO and SiO<sub>2</sub> contents are an accurate reflection of the carbon, manganese and silicon contents of the various heats here described is a strong indication that distribution is being determined accurately.

Certain facts regarding the inclusion content of steels are indicated by this work. The nature of the heats is such that well founded conclusions may not be drawn but certain broad tendencies are indicated. The prominence of FeO even in the steels killed with high manganese and silicon is striking. In silicon-killed steels particularly, FeO is so much higher than would be expected that it probably represents FeO in the sulfides and in solution in the steel. It should be particularly noted that the value given by the FeO analysis must be considered as that for total FeO and not necessarily only that part of the FeO that is combined with the silica. Another significant feature of the analyses is the low MnO content, particularly in view of the fact that the total oxygen contents of the steels are lower in proportion to the manganese content. This, together with the fact that the intermediate manganese steels have higher MnO content than the high-manganese steels and that MnO has been largely eliminated in the higher manganese steels, supports the theory that manganese tends to reduce total oxygen by elimination of MnO.

In heats 5 and 6, A, B and C, however, the MnO is even lower than might be expected, indicating a loss of MnO in the rimming action, which took place during the solidification of these heats. The loss of MnO in this way indicates that the reaction between manganese oxide and carbon takes place preferentially to that between iron oxide and carbon, in which event MnO may be an important factor in the rimming reaction. In view of the high MnO content of the normal range of carbon and manganese rimming steels, the possible commercial significance of this type of analysis is obvious.

Practically all killed steels are treated with silicon in the ladle. It has been argued that large proportions of the silicates formed at this time remain in the steel, but data given here on steels killed with substantial amounts of silicon show that this is not necessarily true. The total oxygen content is low in all of the silicon-killed steels and varies little with wide differences in analysis, indicating that substantial elimination of silicates has occurred and that a steel that has been cleansed by initial deoxidation is not made dirty by a ladle addition. Silicon addition, however, does change the distribution of the oxygen between the various oxide-forming constituents. The FeO content is diminished as the silica content rises, rendering the inclusions less plastic. Thus they are elongated less during rolling, thereby reducing the effective inclusion content. It has been found<sup>4</sup> that the visible inclusions in rolled steel are proportional to the sum of the metallic oxides divided by sulfur. Where the inclusion condition and iodine analysis have been correlated, the results have been promising and indicate that the iodine method can be used to advantage as a guide and criterion of the desired nonmetallic condition.

#### THE OPEN-HEARTH PROBLEM

Present practice in making quality steels gives results in accord with the above reasoning. The first step generally considered in this practice

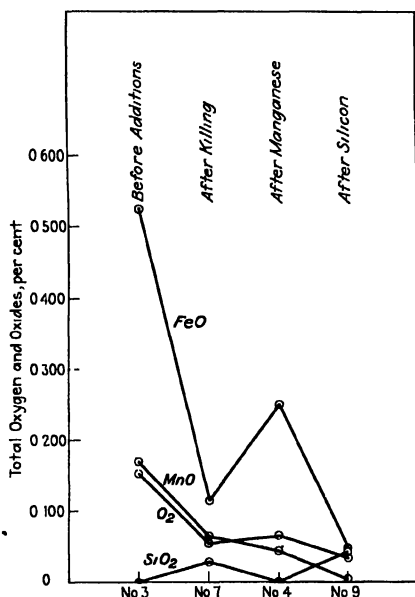


FIG. 2.—EFFECT OF DEOXIDIZERS ON TOTAL OXYGEN AND OXIDES.

is the silicomanganese addition. The state of the heat just before this addition is made compares with that given in heat 3 of the table, due

<sup>4</sup> A. B. Kinzel and W. Crafts: *Trans. A.I.M.E.* (1931) **95**, 143.

allowance being made for carbon content. Immediately after the silico-manganese addition, inclusions are eliminated and the heat is simultaneously reoxidized by the slag. The metal then compares with heat 7. Manganese is then added and the heat tapped shortly thereafter. At this time the state of the metal is similar to that of No. 4. In the ladle, ferro-silicon is added, cleaning the heat. At this, the final stage, the metal is in a condition comparable to heat 9. The variation in total oxygen as well as distribution of the oxygen between the silicon, manganese and iron is illustrated in Fig. 2.

### CONCLUSIONS

1. The iodine method gives total oxygen values which check accurately those obtained by the aluminum method for plain carbon and manganese steels. It should not be used in connection with steels containing the stable carbide-forming elements.

2. The distribution of the oxygen between the various oxide-forming elements, as determined by the iodine method, is in agreement with present ideas on the mechanism of steelmaking reactions and is in line with present practice in manufacturing quality steels.

3. The iodine method may be used as an index of the cleanliness of steels by suitable evaluation of the ratio of  $\text{SiO}_2$  to  $\text{MnO}$  plus  $\text{FeO}$  with respect to the total oxygen and sulfur contents.

4. The practicability and ease of application of the iodine method make it an admirable tool for the use of the steelmaker.

### ACKNOWLEDGMENT

The authors wish to express their appreciation of the interest and assistance given by the officers and members of the Union Carbide and Carbon Research Laboratories, Inc. Messrs. T. R. Cunningham and J. R. Price deserve special mention and recognition for the analytical work, and thanks are also due Mr. R. H. Dunlap for generous assistance in preparing the material.

### APPENDIX.—EXTRACTION PROCEDURE FOR MODIFIED IODINE METHOD

#### *Preparation of Ferrous Iodide Solution*

Five (5.000) grams of plain-carbon steel drillings with silicon content not over 0.03 per cent are transferred to a 300-c.c. Erlenmeyer flask containing 25 c.c. of cold water, 4 grams of ammonium citrate and 30 grams of pure iodine. The flask and its contents are twirled in ice water as described under "Solution of the Sample," until the steel has practically all dissolved. Thirty (30) grams of additional iodine are introduced and the shaking is continued until all iodine has dissolved, at which time the solution is filtered. The total volume of the filtrate and washings should not exceed 75 c.c. This amount of ferrous iodide is used to treat 5 grams of drillings or a 5-gram solid piece of steel. Should the drillings or solid piece treated weigh more than 5 grams, the ferrous iodide should be increased proportionately.

*Solution of the Sample*

From five (5.000) to ten (10.000) grams of the carefully prepared drillings or solid piece of steel are treated with from 75 to 150 c.c. of ferrous iodide solution in a 300-c.c. Erlenmeyer flask. The stoppered flask is placed in ice water and twirled continuously until the sample has dissolved almost completely. The flask is then placed in a shaking machine (run at a low speed) until the metal has dissolved completely, then the solution is filtered immediately on an 11-cm. filter paper of close texture containing a small amount of ashless paper pulp. The filter paper and residue are washed from 18 to 20 times with cold, 2 per cent ammonium citrate solution to remove ferrous iodide, followed by hot 2 per cent ammonium citrate to remove all iodine, and ignited in a platinum crucible first at a low temperature and finally at 1000° C. in an oxidizing atmosphere, cooled in a desiccator and weighed. The percentages of silicon that usually occur in steel do not interfere. However, if desired, after several washings to remove ammonium citrate, the residue may be washed with approximately 50 c.c. of 5 per cent KOH, then thoroughly with hot water, and ignited.

*Analysis of the Residue*

At this stage the residue from the iodine extraction is ready for analysis for the  $\text{SiO}_2$ ,  $\text{MnO}$ ,  $\text{FeO}$  and  $\text{Al}_2\text{O}_3$ . As these methods are standard, they will not be detailed here. For detailed description of the methods actually used at the Union Carbide and Carbon Research Laboratories, the reader is referred to the paper by Cunningham and Price.<sup>5</sup>

## DISCUSSION

(George B. Waterhouse presiding)

C. H. HERTY, JR., Pittsburgh, Pa. (written discussion) —The authors' procedure in determining the application of the iodine method to oxide analysis in steel is to be highly commended. When the results reported in this paper are studied in conjunction with the cited paper by Cunningham and Price, the general method of attack will be found to be sound. We would like to offer three comments in constructive criticism:

1. The size of sample used. On a 5-gram sample a reported analysis for  $\text{SiO}_2$  of 0.004 per cent is the result of the weighing of 0.2 mg. of  $\text{SiO}_2$ , and with such small amounts the accuracy of the method is certainly open to question. It is obvious that if such a small amount of silica is found, the steel may be classed as clean as far as silica is concerned, but that extensive discussion as to factors causing variations in these small amounts is hardly warranted. I have in mind the discussion on page 173, regarding the  $\text{MnO}$  content in heats 5 and 6. It would seem that in order to discuss with confidence the causes of variation in small percentages of any of the oxides a much larger sample should be used.

2. In Cunningham and Price's paper a series of iron-manganese silicate slags was described on which the authors found no attack by the iodine solution. Inasmuch as we are at present using a combination of the electrolytic and the iodine method, we were interested in the attack on the various oxides, and our findings indicate that while many slags are unattacked there are slags that are attacked to some degree. As an example: a large number of inclusions easily visible under the binoculars were extracted from a small test ingot killed with manganese-aluminum-silicon alloy. The extracted inclusions were then given the exact treatment described in this paper and after the treatment it was found that a 20 per cent loss in weight had occurred. The analysis of this particular group of inclusions was:  $\text{MnO}$ , 46 per cent;  $\text{SiO}_2$ ,

<sup>5</sup> Reference of footnote 1.

30 per cent;  $\text{Al}_2\text{O}_3$ , 12 per cent;  $\text{FeO}$ , 12 per cent. I cite this to indicate that whereas most slags may be unattacked there may be others where some modification of the method is necessary.

3. Type of sample used. In a great many instances it is desirable to use samples from particular locations in the steel under investigation and from the standpoint of accuracy a large solid sample is preferable to a smaller sample of drillings. The larger the sample, the more expensive becomes the iodine method. By using a combination of the electrolytic and the iodine method we have been able to obtain very satisfactory results and we believe that such a combination is superior to the use of either method alone.

It is interesting to see that three methods, the aluminum method, the iodine method and the electrolytic method, which have been perfected in the last few years are being used in various combinations. I believe that it is by such combinations that our most rapid development in further researches in steelmaking problems will be made.

A. B. KINZEL.—First, as to the matter of weighing and the size of the sample involved, it should be realized that the type of work to which inclusion analysis applies is today very far from what can be called routine analysis. There is no method that I know of that can be applied on the same basis as the present carbon, manganese, silicon, phosphorus and sulfur determinations which are run through steel-mill laboratories in a routine manner. The weighing of 0.2 mg is not a difficult task for an experienced analyst. In our procedure it is interesting to note that when the sample is ignited the total oxides are usually weighed. The individual analyses are then made and the total of the individual weights invariably checks the total of the residue before the analysis within a tenth of a milligram. No great difficulty has been found in this matter but if there is difficulty in weighing closely, a larger sample may be taken.

With regard to the type of sample, drillings speed up the action, so that a 10-gram sample of a steel comparatively low in carbon will dissolve in about 3 hr without constant attention. Three hours is not considered to be a long time for analysis of this type.

As far as the expense is concerned, we are now redistilling the iodine and collecting it, so that becomes a minor factor. The main expense on the whole job is the iodine itself. I am sure that is what Dr. Herty had in mind. By redistilling and collecting the iodine, that objection has been eliminated.

It is realized that conclusions cannot be based on analysis with differences of 0.002 per cent and conclusions with respect to  $\text{MnO}$  have been drawn from Table 1, where there are really three groups of  $\text{MnO}$  classifications; one where the values run from 0.002 to 0.005 per cent; one in which they run from 0.013 to 0.040 per cent, and then the very high value of 0.170 per cent; and it is those differences in order of magnitude that were used as a basis of the discussion rather than any differences between 0.002 and 0.003 per cent.

Regarding the matter of attack on various types of slags, we have not shown that every alumina, silica, etc., type of slag is unattacked. As a matter of fact, we believe they are all attacked. It is very probable that most of the inclusions are far from simple, and contain sulfur, for example. Yet in the iodine method the sulfur comes down quantitatively as elemental sulfur. As it is in the inclusions originally and is precipitated as elemental sulfur, we think it is possible that what has happened is that the oxide is either hydrolyzed or precipitated as oxide. In the final analysis, the metallic content of the inclusions is accurately registered whether the inclusions are attacked or not attacked during the process of analysis.

The only indication we have that hydrolysis is occurring is that, even though the inclusions in the residue do not look like the inclusions in the steel, the check values



on these split heats obtained from the alumina analysis show that the total corresponding oxygen is being obtained by the iodine method with a high degree of accuracy.

Great care must be taken in sampling, especially if samples of steel are being taken during the time when a reaction is occurring. The sample as finally poured, be it poured in brine or in small ingots or some other way, is really representative of the metal. In the analysis of a given piece of steel that has already been cast or rolled, the difficulty does not arise.

Another thing that should be emphasized is that the total oxygen figures obtained here are surprisingly high in connection with steels containing high silica. It is very probable that we are reporting by the iodine method total oxygen, that is, oxygen in solution as  $\text{FeO}$ , etc., as well as the oxygen in inclusions. That is indicated by the fact that the steels made without any silicon addition, which are comparatively clean under certain circumstances, still give high values.

J. T. MACKENZIE, Birmingham, Ala.—I think Mr. Kinzel misses the point a little on this argument about silicon. There is, of course, no trouble in weighing 0.2 mg. of silicon or silica on a microbalance. But the solubility of the silicon in solution is the point at issue. If there is enough hydrochloric acid solution to take up the ordinary fusion of a mineral of that weight, it would require, I should say, at least three evaporations to dryness to approach the order of accuracy of a thousandth of one per cent silicon, and then I do not know any analysis that would be right sure of that last decimal place. It is not discrediting the method at all.

A. B. KINZEL.—This question resolves itself into a matter of what accuracy is desired; that is, for example, 0.004 per cent plus or minus 0.001 per cent or 0.004 per cent plus or minus 0.0001 per cent. However, if it is satisfactory to say it is 0.004 per cent plus or minus 0.001 per cent, then the method as used is satisfactory, and there seems to be very little need for greater accuracy at present.

R. S. DEAN, Washington, D. C.—It seems to me that the authors have made out an excellent case for the use of this method for total oxygen; that is, comparing it properly with the  $\text{Al}_2\text{O}_3$  method. The question in my mind is whether we can distinguish the separate inclusions. Particularly, we keep talking about  $\text{FeO}$ . We certainly know that under steelmaking conditions, any inclusions we have are not  $\text{FeO}$ . Depending on the percentage of silica, there is a certain amount of  $\text{Fe}_2\text{O}_3$ . I think it is about 11 per cent  $\text{Fe}_2\text{O}_3$  that is in equilibrium with solid iron which drops to 4 per cent of  $\text{Fe}_2\text{O}_3$  with a considerable amount of silica.

The question in my mind is that if there is a certain amount of  $\text{Fe}_2\text{O}_3$  there and a certain amount of  $\text{FeO}$ , what happens to it when it gets into an iodine solution? Would we get anywhere if we attempted to analyze the inclusions extracted by the iodine method for  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ ? In other words, if we want to determine, as we do in certain cases, whether the slag as inclusion was in equilibrium with the metal or not, if we take the inclusions extracted by iodine and analyze them, assuming that we can, for  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ , do we know whether the state of oxidation would be changed by soaking in the iodine solution?

A. B. KINZEL.—We do not know whether it will or not. As a matter of fact, as stated previously, the analysis we are getting for the iron oxide is total; it is not only the iron oxide in the inclusions, it is also that in solid solution. There is no way of differentiating them as yet. However, in view of the fact that this is the first time we have been able to get iron oxide at all, we think we have made one step in the right direction.

You probably realize that the method of analysis is to determine the metal combined with oxygen. We assumed and calculated the metallic content of the residue to

FeO and MnO. This may be wrong, but at least it is something we can reproduce and which we can correlate with other known factors or unknown factors of the steel-making operation.

C H HERTY, JR.—Actually, Dr. Kinzel, are we not reporting on the total iron in the inclusions not only tied up with oxygen but also tied up with sulfur? For example, on an iron very low in manganese, if you have FeS out and you get that in your extraction, you will report the iron present, will you not?

A B. KINZEL.—No, that was one of the great difficulties of some of the other methods, as you know. In this method, we have checked it back and forth and there are some data in the paper that will help clear it. Actually what happens is that the sulfur comes down quantitatively and the iron tied up with the sulfur goes into solution and does not come down in any way. The same is true of the manganese and manganese sulfide.

J. JOHNSTON, KEARNY, N J.—In this paper the authors record a positive advance in knowledge of this elusive general subject. The concordance between their results by this iodine method and by the aluminum method does not however prove absolute that both are quite accurate: the same type of error might affect both, though in general it would probably be only a relatively small correction. For instance, one might not get all the silica in the one case, as mentioned by Mr. Mackenzie, or all of the alumina, in the other, if some of the particles are so very fine that they pass through the filter. Further work on this point would be required before either of these methods could be regarded as an absolute method; in any case this detracts very little from its usefulness, as we are at the moment much more interested in results which are reproducible, even if they should not be absolutely accurate.

I hope that it will soon be possible to arrange for really comparative analyses of oxygen, nitrogen, etc., in steel, to be made by various laboratories, on a number of identical samples, by one or other of all the methods proposed hitherto. This comparison seems to me to be a matter of considerable importance to us all, for it is clearly beside the point to make long series of analyses by any of these methods until we are a little less uncertain as to the precise significance of the results obtainable. The general proposal is to have carefully made samples distributed to any laboratory in position to collaborate on this matter, under the auspices of the Bureau of Standards, which would collate the results. Some have already expressed their willingness to take part, and we anticipate no difficulty in securing the requisite cooperation. It would, however, be helpful if the Iron and Steel Division would formally endorse this project and accordingly I shall later submit for your consideration and action an appropriate resolution.

A B KINZEL—Anyone who has done much work with this solution will realize that filtration itself is not an easy matter. The type of sludge is such that it is very difficult even to get the liquid off; that is, compared to the usual filtration process. We have taken the solution after filtration and inspected it in the ultramicroscope as compared with distilled water, and we find the same order of magnitude in the number of particles, indicating that the filtration is fairly effective. As a matter of fact, from what I have seen of it, I believe that what gets through is of a very low order of magnitude. However, it may be that all of these particles that are extremely small go into solution; alumina, silica, etc., in which case the value is not correct as an absolute value but is correct comparatively.

As Dr. Johnston says, for our purposes it really does not make much difference whether we are losing a little bit or not, provided we lose the same amount all the time.

There is no way of proving the absolute status of either of these tests at the present time, to the best of my knowledge. The fact that they check as closely as they do renders the probabilities of their absolute value comparatively high, and if the absolute value is wrong, it is highly probable that the differences between the values reported and the absolute values are extremely small and would probably be less in order of magnitude than the errors with which we work.

The program suggested by Dr. Johnston is certainly meritorious. I had the privilege of discussing it with him yesterday, and I am sure that practically all the laboratories that have been doing this kind of work will consider it a privilege to cooperate and will feel that we are all getting the same kind of benefit. I certainly hope that when this is taken up at the business meeting it will receive the expected enthusiastic support.

H. S. RAWDON, Washington, D. C.—I would like to refer to the point that to me is of the greatest interest in the paper; that is, the results that are summarized in Fig. 2. I am assuming that the method is all that is claimed for it, and that the four heats that are given here are representative of the different conditions of the metal, after the manganese addition and after the silica addition. It seems to me that they are of very decided interest in showing the relative value of the total oxygen determinations and the determination of distribution of the oxygen.

It will be noted from the data that after the metal has been killed the oxygen content is practically constant regardless of subsequent treatment. I will not say that this is absolutely true, but there seems to be no great variation in the total oxygen content. There is, however, a decided difference in the distribution of the oxygen. If one should make a simple oxygen determination and get total oxygen content, he would probably conclude that there is very little difference between the three heats. That there is a decided difference, however, is shown by the results of the additional work which establishes the distribution of the oxygen. It seems to me that that is the point that must be strongly emphasized and recognized by workers in this field.

In spite of all that has been done and said to the contrary, a good many metallurgists still feel that a total oxygen determination is going to tell the story in establishing the difference between certain heats of steel. As a matter of fact, that is just the beginning of the story. One must depend on some such method as this, a residue analysis method, to show how that oxygen is distributed through the metal and to tell just how such heats do differ from one another. If this modified iodide method will tell us that, it certainly ought to find a good many useful and valuable applications.

P. H. BRACE, Pittsburgh, Pa.—This matter of solid-solution oxygen is puzzling. Considering the first analysis, we find a total oxygen content of 0.17 per cent reported. It might be interesting to add to the data that have already been presented, in answer to other questions, information as to whether the oxygen was present mainly as inclusions or in solid solution. The difficulty that I have is in imagining oxygen in solid solution and visualizing the physical form of that oxygen after the iodine procedure has been completed. If you visualize oxygen in real solid solution and take away all the iron, where is the oxygen?

A. B. KINZEL.—What it amounts to, as I see it, Mr. Brace, is an explanation of the mechanism of the iodine reaction, and I cannot give one.

P. H. BRACE.—It is more than that. You have a certain sludge, we will say, from analysis 1. Is this composed of globules of oxide which have been formed from the molten iron-oxygen solution as inclusions or is it real sludge, we will say colloidal

sludge such as might be expected to result from the removal of the metallic portion of an iron-iron oxide solid solution?

A. B. KINZEL.—Both.

P. H. BRACE.—It might be that your ultramicroscope or possibly X-ray methods applied to that sludge would give some interesting information as to the constitution of the residue of oxides that you have extracted from solid solution.

A. B. KINZEL.—That is true, and I think it is entirely worth doing. One objection is that the inclusions as they exist in that sludge are probably not the inclusions that exist in the steel; in fact, we have good grounds to believe they are not. That is the reason we have not pushed that end of the investigation sooner.

MEMBER.—In examining sludge or residue under the microscope, do you find that the inclusions seem to be compounds of various sorts mixed together? Under the microscope you see the inclusion, but you will see that inclusion apparently made up of one, two, sometimes maybe three constituents. Do you see the same thing in the residue?

A. B. KINZEL.—In the iodine residues that we have had, we have found a few clean-cut inclusions, but as we have had strong indications that the inclusions are broken up in extraction, we have not investigated it further. We believe that in the steel the inclusions are made up of complex solutions such as sulfides and oxides of manganese, iron, aluminum and silicon, existing in one inclusion. Yet on the analysis the sulfur is taken out of that inclusion and precipitated as elemental sulfur, so that the physical nature of the inclusion has certainly been changed.

D. L. RECK, Middletown, Ohio (written discussion).—The iodine method is a valuable tool in identifying certain oxides in a sample of steel. However, it is not a universal method, and the results are reliable only when interpreted in light of the limitations. No conclusions concerning the accuracy of determining the distribution of the constituent oxides should be drawn from the agreement between the total oxygen results obtained by the iodine method and those obtained by the alumina residue method. In fact, the method of preparing the samples is open to objections that make some of the results open to serious question.

When liquid metal is thrown into water, the resulting solid metal is somewhat porous and full of small cavities caused by shrinkage of the metal during cooling. Some of these pores penetrate deeply from the surface toward the center. Water and steam enter these pores and react with the iron to form iron oxide. Thus, not only would the surface of the pellets be covered with iron oxide before sand blasting, but also the inner metal, which was used as a sample, would be contaminated with oxides not originally present in the liquid iron. Even though the pellets were examined under the microscope after sand blasting to make sure they were free from iron oxide, the sand blasting would have a tendency to cold-work the surface of the pellets and cause the metal to flow over the pores or holes, which were previously filled with oxide by reaction with the water and steam. Although the metal appeared perfectly clean on the surface, the oxides hidden in the pores would be recovered by the iodine method, causing the iron oxide results to be too high. The chilled shot used for a sample must have contained some blowholes caused by the reaction between MnO and carbon, which the authors describe. Visual examination of the interior of the shot would not indicate whether oxides in the blowholes were deposited there by rimming action or were formed by water and steam. Conditions under which the samples were prepared would indicate that both are possible.

If extreme care is not used in adding aluminum to the samples, the oxygen results obtained by the alumina residue method will be unduly high, owing to atmospheric oxidation of the aluminum. This is especially true of low-carbon rimming steels.

Cunningham and Price have confirmed previous knowledge<sup>6</sup> that certain iron and manganese silicates are insoluble in the iodine solution used as a solvent for metallic iron. Thus, the iodine method can be relied upon to recover certain iron and manganese oxides which are present in the form of silicates.

In the range of composition represented by samples 1, 1-A, and 2, reported in the paper under discussion, the vacuum fusion method is widely recognized as a reliable means of estimating total oxygen, and could well be used as a reference method to overcome two difficulties encountered using the alumina method for comparison:

1. The sample for both methods could be taken from the same piece, and thus elimination of oxygen during solidification would not be objectionable. This would remove the difficulty of securing rapidly chilled shot.

2. High sulfur probably would have no interfering influence.

Our experience with the iodine method, including modifications, has been such that we cannot accept it as a universal method for solid oxide inclusions. However, it is satisfactory for certain constituents. Silica, alumina, and certain types of silicates may be determined satisfactorily. For other constituents we cannot accept the results obtained by the present form of the iodine method.

F. G. NORRIS, Middletown, Ohio (written discussion)—Messrs. Egan, Crafts and Kinzel have presented a welcome contribution to the published knowledge of the inclusion content of a series of induction furnace heats. The assumption that selected induction furnace heats represent successive samples from the open-hearth bath has led to difficulties and possible inconsistencies. Use of a pure iron oxide slag tends to make the total oxygen higher than that of samples of the same metallic composition taken from an open-hearth bath. This tendency is shown clearly in samples 1 to 3, which contain total oxygen well above that found in an open-hearth bath of this carbon, manganese and silicon content. I doubt that any commercial charge now used in basic open-hearth practice results in 0.27 per cent residual manganese in a bath containing 0.15 per cent total oxygen. Certainly this composition does not represent "present practice in making quality steels."

The implication that the increase of 26 points of manganese (from 1.24 to 1.50 per cent) resulted from a ladle addition of ferrosilicon requires some comment. I suggest that the hypothetical ladle addition was equal weights of ferromanganese and ferrosilicon.

Considering further the authors' reconstruction of a hypothetical heat, comparison of sample 4 with sample 9 shows that not over 0.20 per cent silica was possible from oxidation of silicon by MnO and FeO. Probably not this much was formed because some MnO and FeO would be eliminated as silicates rather than reduced by silicon. Of this possible 0.20 per cent silica formed, 0.044 per cent remained, either suspended or dissolved in the steel. Whether 80 per cent or less elimination of silicates is good enough so that the product can be called clean steel is a matter of judgment. Does the statement that "substantial elimination of silicates has occurred" mean that most of the oxides found in samples 8 to 14 were in solution in the liquid steel?

The value of a method for identification of the several oxides is shown by a comparison of sample 4 with sample 9. The alumina method indicates a drop in total oxygen from 0.07 to 0.038 per cent, and using this method alone one would conclude that the difference was due to a cleaning effect. Results of the iodine method indicate that the silicon added to sample 9 has reduced the MnO and FeO with an accom-

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<sup>6</sup> Reference of footnote 1.

panying increase in silica. Whether a change from 0.002 to 0.044 per cent silica is beneficial must be determined experimentally, and whether beneficial or not, can scarcely be termed a cleansing. The use of the results of the iodine method as an index of cleanliness is mentioned in conclusion 3, but is not described elsewhere in the paper. Further details would be welcome.

What is considered the typical composition of a heat "cleansed by initial deoxidation"; and, more specifically, does sample 4 represent such a heat? I believe that a ladle addition of ferrosilicon made to a heat containing 0.07 per cent total oxygen would leave a substantial percentage of silicates in the steel. This is only an opinion, however, and is not based on results of samples taken before and after ladle treatment.

Although I agree that the MnO content of molten steel may be decreased either by reduction of MnO or by elimination of MnO-bearing inclusions, the reasoning by which the authors come to this conclusion is not supported directly by the evidence presented. I object especially to the suggestion that MnO is reduced by carbon, thus causing a rimming action in chilled shot. Several exceptions to the statement that "the intermediate manganese steels have higher MnO content than the high-manganese steels" are found in Table 1. Comparison of sample 5 with samples 6A, B, and C shows that an increase from 0.50 to 1.50 per cent manganese does not affect the MnO content of high-carbon low-silicon steel. Comparison of sample 8 with sample 9 shows that a similar increase in manganese does not affect the MnO content of low-carbon silicon-killed steel. Comparison of sample 11 with sample 13, and of sample 12 with sample 14, shows that an increase in manganese does not affect the MnO content of high-carbon steel containing either 0.30 or 0.80 per cent silicon.

A hint of the cause of the variation of the MnO content is given by comparing sample 7 with sample 8, both of which are the same in carbon and manganese, but differ in silicon. Following this clue, the low MnO content of samples 8 to 14 can be attributed to the high silicon content. Samples 5 to 6C indicate that also high carbon may be effective in reducing MnO.

I believe that MnO was reduced before the heat was poured and that reaction of MnO with carbon to produce rimming during solidification of small shot chilled in brine is unlikely. This type of solidification is different from that of a 2½-ton rimming ingot in that the conditions under which the commercial ingot solidifies are more favorable for reaction. The conclusion that during the rimming action MnO is mechanically eliminated rather than reduced by carbon is supported by the common observation that manganese (total) is higher in a killed sample than in a rimmed sample and that a high-manganese oxide scum accumulates on top of a rimming ingot.

J. J. EGAN, W. CRAFTS and A. B. KINZEL (written discussion).—The authors appreciate Mr. Reck's description of the difficulties of preparing steel shot. However, it is believed that with reasonable care representative samples may be obtained. If scale were present on the samples, it could hardly have been expected that such close check results could have been obtained, which in turn checked closely the alumina extraction. With respect to the use of the vacuum fusion method, although it is of great value for many applications, the authors' experience has been that it is not accurate and that the total oxygen content is of little significance in the analysis of steel. Although the iodine method is subject to certain limitations, so that Mr. Reck is hardly justified in calling it a universal method, we have obtained reasonable and consistent values for FeO and MnO as well as for the less soluble SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.

Mr. Norris' well considered comments on the implications of the analyses rather than the iodine method itself have been read with interest. The authors agree that

the total oxygen content of these steels was in general higher than would be found in open-hearth steels of the same analysis. However, the reactions produced by deoxidizing additions are not greatly affected by the higher oxygen content, so that these heats have served to indicate relative results, even though the actual oxygen contents are not typical of open-hearth steels. Therefore, although substantial elimination of silicates has resulted from the additions, the actual oxygen content was still high owing to the method of making the steel, in this case about three or four times as high as would be found in similar open-hearth steel.

While carbon and silicon are obviously more effective than manganese in reducing the MnO content of the steel, heats 3 and 4 definitely indicate the higher MnO content of intermediate manganese steel where the MnO content is sufficiently high to be significant. In the higher carbon and silicon steels the MnO has been reduced by the deoxidizers to such a low value that the manganese content is not effective. In the high-carbon, low-silicon heats 5 and 6 the MnO was lower than had been expected, leading to the opinion that carbon had reduced MnO during the rimming reaction. As stated in the paper, this is only an opinion that cannot be proved from the available data. Although the rimming reactions in small shot and large ingots are somewhat difficult to compare, the authors have seen little to indicate any significant difference other than the extent to which the reaction is carried. It is true that in large ingots, although some MnO is carried off, probably in slag that came primarily from the refractories, the amount is small compared to that of MnO eliminated. Our opinion of the reduction of MnO in the rimming reaction has also been strengthened by analyses of commercial rimmed steels where it was found that in steels of practically the same analysis the MnO content was reduced to a constant value, but that over-rimmed steel had a low FeO content while under-rimmed steel had a high FeO content. Although this is believed to indicate that MnO is reduced preferentially to FeO, it is realized that the data are inadequate to reach a sound conclusion.

In heat 9, which contained silicon, the oxygen was about 50 per cent lower than in heat 4. The inclusions in the former, consisting primarily of 0.044 per cent  $\text{SiO}_2$ , will undoubtedly make an effectively cleaner rolled bar than the inclusions of heat 4 containing primarily 0.250 per cent FeO. This is due not only to the reduction in total oxygen but to the fact that high-silica inclusions will elongate to a much smaller degree than the more plastic high-FeO inclusions. When the composition of the inclusions is evaluated, the degree of elongation has been found to give accurate estimate of the inclusion content as determined by inclusion counts. This has been illustrated in work on the mechanical effect of inclusions.<sup>7</sup>

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<sup>7</sup> A. B. Kinzel and W. Crafts. Inclusions and Their Effect on Impact Strength of Steel. *Trans. A.I.M.E.* (1931) **95**, Iron and Steel Div., 143.

## Analyses of Inclusions in High-carbon Tool Steels

BY HAAKON STYRI,\* PHILADELPHIA, PA.

(Buffalo Meeting, October, 1932)

IN discussion of Dr. Fitterer's paper on electrolytic separation of slag inclusions, some results from experiments on electrolyzing high-carbon steels at the SKF Research Laboratory were given.<sup>1</sup> We had been working for a number of years on chemical methods of separating the inclusions but could not find any solvent that would dissolve the steel without attacking some of the inclusions, particularly the sulfides in which we were mostly interested at the time, nor any that would dissolve all sulfide or silica in filings as fine as 300 mesh without attacking the iron. Electrolytic methods had also been tried without any real progress until we learned from the Bureau of Mines about the use of the collodion membrane around the anode. Our early difficulties were to some extent different from those of the Bureau of Mines, perhaps because of experimenting on steels of higher carbon content, but most of our difficulties were of the same nature as those of the Bureau.

Formation of large quantities of basic hydroxides was traced to the use of impure and oxidized ferrous sulfate. To protect from oxidation from the atmosphere during electrolysis, after purer chemicals were obtained, a thin layer,  $\frac{1}{8}$  in. or less, of molten paraffin was poured over the surface of the cathode liquid, where it solidified. It was found desirable also to hold the cathode chamber slightly acid by initial addition of 0.1 per cent acid (sulfuric or hydrochloric) to prevent precipitation of the hydroxide. This acidity would decrease gradually and the cathode chamber would become neutral before the end of the electrolyzing.

The increase in acidity in the anode chamber during our early experiments had appeared to cause attack of the precipitated sulfides in the residue, which originally was analyzed by volumetric method for sulfur, and for this reason a 10 per cent sodium citrate solution was substituted for the sulfate in the anode chamber.

With the use of the more reliable Eschka method for sulfur determination (as in coke), there was however no serious attack on the sulfides in the anode chamber with a variety of different liquids, as shown in Tables 2 and 4. The Eschka method gives a higher sulfur value than

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<sup>1</sup> H. Styri: Discussion on Electrolytic Extraction of Inclusions from Steel. *Trans. A.I.M.E.* (1931) 95, 212.



the volumetric method. The principal sources of errors in the use of the volumetric method for sulfur is omitting zinc, as shown by Dr. Fitterer,<sup>2</sup> and the fact that sulfides evidently are dissolved in slag particles or included in carbides, so that they are not readily attacked and therefore prolong the distillation of  $H_2S$ . The sulfur is probably combined with both manganese and iron.

Stronger and cheaper cellulose bottle caps from duPont were substituted for the collodion diaphragms and lead cable coated with candelilla wax was used for suspension of the sample.

The steels used in the experiments recorded in this paper have the analyses shown in Table 1. The time used for electrolysis was about 24 hours.

TABLE 1.—*Analyses of Steels Used in Experiments*

Steel No	Composition, Per Cent		
	C	Cr	S
1	0 95	0 16	0 024
2	0 99	0 97	0 014
3	0 94	0 97	0 014
4	0 125	nil	0 06
5	0 755	nil	0 016

The electrolyte used for samples 1 to 11 was 3 per cent crystalline ferrous sulfate plus 0.1 per cent sulfuric acid in the cathode chamber and 10 per cent sodium citrate in the anode chamber; for samples 65 to 74, it was 3 per cent crystalline ferrous chloride plus 0.1 per cent hydrochloric acid in the cathode chamber and various solutions in the anode chamber, and for samples 100 to 155 the same solution in the cathode chamber and 3 per cent ferrous chloride in the anode chamber.

Samples 1 to 11 in Table 2 were annealed carbon steel No. 1. The residue from all of these had a large volume and weighed over 10 per cent of the total amount taken into solution. The analyses show that all the sulfur and all the carbon is found in the residue. Samples 65 to 76 of alloy steel No. 2, annealed, gave even more bulky residues.

Dr. Arne Westgren, of Stockholm, very kindly made X-ray studies of two samples treated in a manner similar to that given for No. 75, and found carbides so predominating that other constituents could not be distinguished easily.

The large amount of carbides was very troublesome in further analyses of the residue and a number of efforts were made to separate the carbides from the other particles by flotation, centrifuging or decantation, but the great variation in particle size and presence of colloidal carbon and  $SiO_2$  and some hydroxides evidently would make such separation very difficult,

<sup>2</sup> *Trans. A I M E* (1931) 95, 215.

TABLE 2.—*Electrolytic Data*

Sample No	Steel	Electrolyte		Weight Dissolved, Grams	Residue, Per Cent of Original								
		Cathode	Anode		Weight	S <sup>a</sup>	Mn	SiO <sub>2</sub>	C	Al	Fe	Cr	
1	No. 1, annealed	3 % FeSO <sub>4</sub> + 0.1 % H <sub>2</sub> SO <sub>4</sub>	10 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub>	25.56	10.5	0.022							
2				21.91	10.7	0.023							
3				24.71	11.5		0.023						
4				21.97	13.5			0.043					
5				19.03					0.95				
11	No. 2, annealed	3 % FeCl <sub>2</sub> + 0.1 % HCl	3 % FeCl <sub>2</sub> (Cryst) + 0.1 % HCl	24.22	10.9		0.019	0.040		0.007			
65				25.28	13.2	0.015							
66				25	13.7	0.014							
67				25.6	15.5	0.015							
73				23.55	15.5	0.015							
74	No. 2, quenched at 1040° C.	3 % FeCl <sub>2</sub> (Cryst) + 0.1 % HCl	3 % FeCl <sub>2</sub> (Cryst)	22.75	15	0.016							
75				24.24	15.6	0.014							
76				21.88	14.4	0.015							
100	No. 2, quenched at 1040° C.	3 % FeCl <sub>2</sub> (Cryst)	3 % FeCl <sub>2</sub> (Cryst)	22.25	3.4	0.011 <sup>a</sup>	0.03				1.17	0.6	
101				18.37	2.6	0.011 <sup>a</sup>	0.03				0.90	0.72	
103				21.10	2.2	0.012 <sup>a</sup>	0.029				0.82	0.56	
104				22.6	4.3				0.61				
105				20.5	3.7				0.59				

<sup>a</sup> Samples 1 to 76 by Eschka method, samples 100 to 103 by volumetric method<sup>b</sup> Volumetric.

TABLE 3.—*Treatment of Residue*

Sample No	Steel	Weight Dissolved, Grams	Residue Treated with	Residue after Treatment, Per Cent			Filtrate after Treatment, Per Cent				
				S <sup>a</sup>	Mn	Fe	SiO <sub>2</sub>	S	Mn	Fe	SiO <sub>2</sub>
78	No. 3, annealed	26 2	10 % (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub> ; 2 hr, room temp.	0 013	0.029		0 006		tr.	0.14	0.21
120		26 35 }	25 % NaOH, 72 hr at 70° C		0 030		0.012		tr.	0.21	0.22
122		23 11 }	Untreated		0 031		0 22				
123		21 16	1 % HCl, 10 min., room temp		0 031	1 7	0 21		tr.	0 14	0.02
132		20 41	1 % HCl, 20 min., room temp.		0 031	1 4	0 20		tr	0 34	0 03
133		24 45	1 % HCl, 30 min., room temp.		0 031	1 1	0 17		tr.	0.67	0.05
136		20 15	1 % HCl, 60 min., room temp		0 025	1 0	0 15		0 005	0.94	0 07
137		16 95	5 % HCl, 20 min., room temp		0 026	0 8	0 16		0 005	0.74	0 06
135		21 45	1 % HCl, 20 min., room temp		0 026				0 001	0 005	
140		25 58	1 % HCl, 20 min., room temp		0 009				0 002		
141		17 65	5 % C <sub>2</sub> H <sub>5</sub> O <sub>4</sub> , 20 min		0 011	0 030			tr.		
142		23 37	20 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub> , 20 min		0 014	0 031			tr.		
143		22 06	50 50 Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub> ; 25 % + 3 % FeSO <sub>4</sub>		0 015	0 03			ml		
144	No. 3, quenched at 1100° C.	23 14	1 % HCl, 10 min., room temp	0 015	0 029	1 7	0 21		tr.	0 017	0.004
145		12 6	1 % HCl, 10 min., room temp	0 015	0 026	1 9	0 19		0 005	0 08	0.02
146		21 88	Water	0 0135							
148		23 1	10 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub> , 10 hr 80° C	0 014	0 029	1 2	0 17		ml	tr.	0 46
150		21 6	10 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub> , 48 hr. 80° C.	0 0135	0 029	0 84	0 05		ml	0 003	0 58
155		20 5	25 % NaOH, 72 hr.				0 007	0 010			0 21

\* Eschka method.

TABLE 4.—*Electrolytic Data*

Sample No	Steel	Electrolyte		Weight Dissolved, Grams	Residue, Per Cent of Original			
		Cathode	Anode		Weight	S*	Mn	SiO <sub>2</sub>
152	No. 3 quenched at 1100° C	FeSO <sub>4</sub> + 1 % NaCl	FeSO <sub>4</sub> + 1 % NaCl	23 40	6 05	0 018 E	0 03	
153	No. 3 quenched at 1100° C	FeSO <sub>4</sub> + 1 % NaCl	FeSO <sub>4</sub> + 1 % NaCl	21 83	9 3	0 011 V	0 0295	
156	No. 4 annealed	FeSO <sub>4</sub> + 1 % NaCl	FeSO <sub>4</sub> + 1 % NaCl	21 75	5 8	0 051 V		0 008
157	No. 4 quenched at 930° C	FeSO <sub>4</sub> + 1 % NaCl	FeSO <sub>4</sub> + 1 % NaCl	26 51	3 5	0 053 V		0 008
158	No. 5 annealed	FeSO <sub>4</sub> + 1 % NaCl	FeSO <sub>4</sub> + 1 % NaCl	21 98	13 4	0 010 V		0 08
159	No. 5 quenched at 930° C.	FeSO <sub>4</sub> + 1 % NaCl	FeSO <sub>4</sub> + 1 % NaCl	20 3	5	0 011 V		0 078
160	No. 4 annealed	3 % FeSO <sub>4</sub>	10 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub>	13 8	13 3	0 052 V		0 025
161	No. 4 quenched at 930° C.	3 % FeSO <sub>4</sub>	10 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub>	17 73	4 02	0 049 V		0 011
162	No. 5 annealed	3 % FeSO <sub>4</sub>	10 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub>	15 8	12 9	0 012 V		0 14
163	No. 5 quenched at 930° C.	3 % FeSO <sub>4</sub>	10 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub>	19 75	4 3	0 014 V		0 16
164	No. 4 annealed	3 % FeCl <sub>2</sub> + 0 1 % HCl kept acid	3 % FeCl <sub>2</sub>	24 28	3 0	0 064 E		0 016
165	No. 4 quenched at 930° C.	3 % FeCl <sub>2</sub> + 0 1 % HCl kept acid	3 % FeCl <sub>2</sub>	18 35	1 9	0 049 V		0 017
166	No. 5 annealed	3 % FeCl <sub>2</sub> + 0 1 % HCl kept acid	3 % FeCl <sub>2</sub>	18 45	8 6	0 015 E		0 17
167	No. 5 quenched at 930° C.	3 % FeCl <sub>2</sub> + 0 1 % HCl kept acid	3 % FeCl <sub>2</sub>	20 1	3 56	0 013 V		0 15
168	No. 4 annealed	10 % CuSO <sub>4</sub>	0 1N KBr + 10 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub>	18 8	2 7	0 043 V		0 011
169	No. 3 quenched at 1100° C.	10 % CuSO <sub>4</sub>	0 1N KBr + 10 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub>	18 0	1 7	0 01 V	0 031	0 19
170	No. 3 quenched at 1100° C	10 % CuSO <sub>4</sub>	0 1N KBr + 10 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub>	22 9	not det.	0 01 V	0 03	0 20
171	No. 3 quenched at 1100° C.	10 % CuSO <sub>4</sub>	0 1N KBr + 10 % Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub>	23 9 <sup>a</sup>	not det.			0 16

\* E indicates Eschka method; V, volumetric  
<sup>a</sup> Washed with 500 c.c. 3 % Na<sub>2</sub>CO<sub>3</sub>, filtrate 0.06 % SiO<sub>2</sub>.

and no satisfactory results were obtained. Magnetic separation was also tried, but possibly the use of too strong a magnet and the large quantity of carbides tended to attract all or most of the particles to the magnet.

Dr. Benedicks recently obtained<sup>3</sup> satisfactory results by using an electromagnet in the form of a needle followed by fractional separation. Such a method seems promising but was not tried in our experiments.

The use of sulfates as electrolyte made it necessary to wash the residue carefully before using the Eschka method for sulfur determination, and to avoid this tedious washing other electrolytes were tried, as shown in Table 2. The use of the separating membrane, of course, facilitated such choice of different electrolytes.

In order to eliminate carbides from the residue, samples were quenched from 900° C., but this was not high enough to bring all the carbides into solid solution, so further tests were made on No. 2 steel after quenching samples in brine from 1040° C. (samples 100 to 105). Some residues from samples treated in this way and electrolyzed in ferrous chloride solutions, like sample 100, were also kindly investigated by Dr. Westgren, who found no carbides present. The tables show that the bulk of the residue was materially reduced by this method.

Some of the carbon is still found in the residue and is probably in colloidal form. Volumetric determination of sulfur (samples 100 to 103) (using zinc) gave lower values than the Eschka method (samples 65 to 76 and 142 to 150), but checked fairly well with volumetric sulfur of 0.012 per cent of original sample. The fact that there is practically complete recovery of sulfur by the volumetric method is proof that it must be present as sulfide.

The amount of manganese, sulfur and silica in the residue calculated in percentage of sample is quite constant for all the different electrolytes. But iron and chromium in Table 2 vary, probably from mechanical contamination, while the iron in tests recorded in Table 3 show less variation.

Further treatments of the residues are shown in Table 3. The weak acids were tried in order to dissolve the hydroxides and evidently some iron may be taken up without serious attack of the sulfur or manganese. The fact that less manganese than sulfur is dissolved indicates that some sulfur is combined with iron. Digesting for a long time with 25 per cent NaOH dissolves all the silica and most of the sulfur but does not take manganese into solution. Digesting with 10 per cent sodium citrate for 48 hr. at 80° C. brings some iron and silica in solution and does not bring sulfides, silica or manganese in solution.

The manganese in the residue is recorded as manganese and not as oxide or sulfide because none of these compounds can be identified by the present chemical analyses. If manganese oxide were present we

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<sup>3</sup>R. Treje and C. Benedicks: *Jernkontorets Ann.* (1932) 116.

should find, according to Fitterer, that at least a considerable amount, if not all, should be in the filtrate from samples 142, 143, 148 and 150, of which the residues were treated with various solutions of sodium citrate after electrolysis with ferrous chloride in the anode chamber. Benedicks found that manganese oxide was more soluble in 2 per cent ferrous sulfate than in 10 per cent sodium citrate, but only slightly soluble in 10 per cent sodium citrate plus 0.1N potassium bromide. Still we find in Table 4 about the same amount of sulfur and manganese in samples 156-7, 160-1, 164-5 and 168 and the same in 162-3 as in 166-7.

The total manganese found in samples 100 to 155 where ferrous chloride was used as electrolyte is about the same as in 169 to 170 using the solutions proposed by Benedicks, namely 0.1N potassium bromide plus 10 per cent sodium citrate in the anode chamber and 10 per cent copper sulfate in the cathode chamber.

By using Benedicks' electrolytes there was no gas evolution, there was no formation of hydroxide and the acidity in the anode chamber was found by Benedicks to increase from pH 7.4 to pH 5.3 after 15 ampere-hours.

In order to facilitate the treatment of the residues, a modification was used, by substituting for the membrane a Whatman No. 50 filter folded around the bottom of a 2-in. glass tube and held with rubber bands. This was used on samples 132 to 150, inclusive. In tests 144 to 150, inclusive, small amounts of hydrochloric acid were added from time to time in the cathode chamber to keep it slightly acid. In the anode chamber the acidity increased gradually during the run with all the electrolytes used.

In our experiments we have studied particularly the behavior of the sulfides, as they were easy to analyze, but we have also tried to identify the other constituents. The values obtained for sulfur, manganese and silica in the residues from different steels show a fair degree of agreement for each steel when using different electrolytes, but evidently more experiments by different laboratories should be compared before any particular method or electrolyte should be standardized.

### SUMMARY

The electrolytic method for separation of inclusions in steel has given satisfactory results when a membrane is arranged around the anode to collect the undissolved particles.

Suitably dense paper filters attached to the bottom of a glass tube may serve better for many purposes than collodion bags, because they permit direct filtration.

A variety of electrolytes may be used, provided care is taken that the cathode chamber is kept slightly acid (0.1 per cent or less), so that hydroxides are not formed on the membrane, and that the anode chamber does

not get too acid so that precipitated particles will be attacked to a disturbing degree.

When it is desired to keep carbides away from the residue, this may be done by quenching the steel from high enough temperature to bring the cementite in solid solution.

Determination of sulfur by the volumetric method, giving practically complete recovery of the sulfur present in the steel, indicates that sulfur is present as sulfide, probably as  $(\text{MnFe})\text{S}$ .

Short-time treatment of residue with weak acids does not seriously affect the sulfides or manganese but does attack some of the iron. Seventy-two hours digesting with 25 per cent sodium hydroxide brings all the silica into solution and also attacks the sulfide. Digesting with 10 and 20 per cent sodium citrate brings a large amount of iron, but only a smaller amount of silica, sulfur or manganese into solution, indicating that the manganese is not present as manganese oxide but probably mostly as silicate.

The amount of iron found in the residue from heat-treated samples is rather constant and probably a large part of it is bound to the slag particles, while the rest is metallic iron or to a small degree hydroxide.

The determination of sulfur by electrolysis and treatment of the residue by the Eschka method is so convenient that it may be used for routine gravimetric analyses of sulfur in some cases where time is of little importance.

The total proportion of silica is very constant, except in samples from steel No. 4, where the quantity is so small that great error in analyses may be expected. Only a small amount of silica is apparently present in form of colloidal silica, as treatment with hot 3 per cent sodium carbonate takes some in solution.

#### ACKNOWLEDGMENTS

All the analyses of these experiments were made by Mr. E. H. Smith of the SKF Research Laboratory. The author wants to express his great appreciation for the care and patience exercised by Mr. Smith in making these tedious analyses, and for the kindness of Dr. Westgren in examining some of the samples by X-ray.

#### DISCUSSION

*(George B. Waterhouse presiding)*

A. B. KINZEL, New York, N. Y.—Dr. Styri has made remarkable and practical changes in the electrolytic method. Regarding the extraction method in general, it has always seemed to us that any method that fails to determine iron oxide may be interesting and instructive, but should be considered only as a step toward the solution of the problem in which we are interested. The electrolytic method as yet gives us no hope in respect to the determination of iron oxide. Perhaps Dr. Styri has done

work on this phase of the problem; if so, it would certainly be illuminating to hear from him. At the Union Carbide and Carbon Research Laboratories, we have been working with the iodine method and believe that this is now in such a state of perfection that it may be used with assurance in connection with steels that do not contain the stable carbide-forming elements, such as chromium, tungsten and vanadium.<sup>4</sup>

P. H. BRACE, East Pittsburgh, Pa.—I am going to ask the chairman's indulgence of a departure from the subject matter of this interesting paper on the analysis of inclusions. We are much interested in the effects of inclusions and I would like to have Dr. Styri, if he will, tell us what his views are as to the nature or quantity of inclusions that can be permitted in high-tensile steels intended for heavy service without causing unreliability directly traceable to the inclusions.

H. STYRI.—In regard to iron oxide, the study in Stockholm possibly shows the way out. I believe Dr. Benedicks separates the carbide magnetically, and of course he also gets metallic iron out. However, it is a question whether he gets it out quantitatively. Metallic iron is taken out by treating the residue with copper sulfate, precipitating the copper, whereafter the copper is dissolved in KCN solution. Remaining Fe in the residue should be combined iron and is determined chemically.

A. B. KINZEL—Hydroxide.

H. STYRI.—We do not get hydroxide by his method and, of course, not by the slightly acid solutions we have been using.

I agree with Mr. Kinzel that it is necessary to determine the iron oxide content in order to know what happens, but much can be learned even by studying silicates and sulfides, which probably in our samples have been in solid solution.

Regarding the effect of inclusions on the quality of material, it depends on what the material is going to be used for, where we should draw the limit. I thought some years ago that it was very important to get rid of inclusions in order to increase the life of the material. Later on I had to realize that the presence of even noticeable inclusions does not seem to affect the endurance. There are other things that are much more important. Of course, I do not now talk about large masses or agglomerations of inclusions, but separate microscopic inclusions, glassy with no sharp corners. Crystalline inclusions such as alumina are probably much worse if they are present even as very small inclusions.

G. R. FITTERER, Pittsburgh, Pa. (written discussion).—Subsequent to the presentation of my paper<sup>5</sup> on this subject before the Institute, three publications have appeared which have recommended electrolytes of widely varying natures. Besides this paper of Dr. Styri's, these include Scott's<sup>6</sup> magnesium iodide electrolyte and Treje and Benedicks'<sup>7</sup> potassium bromide solution. The "laboratory manual" type of paper that I presented last year was written for the steel-plant analyst and has been

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<sup>4</sup> See page 169, this volume.

<sup>5</sup> G. R. Fitterer: Method for the Electrolytic Extraction of MnO, MnS, FeS, and SiO<sub>2</sub>, Inclusions from Plain-carbon Steels. *Trans. A. I. M. E.* (1931) **95**, Iron and Steel Div., 196-208.

<sup>6</sup> F. W. Scott: Extraction of Slag and Oxide Inclusions in Iron or Steel. *Jnl. Ind. & Eng. Chem., Anal. Ed.* (1932) **4**, 121.

<sup>7</sup> R. Treje and C. Benedicks: Method for Electrolytic Slag Determination in Iron and Steel of Low Carbon Content. *Jernkontorets Ann.* (1932) **4**, 165.



followed by a Bureau of Mines paper describing all of the characteristics of the ferrous sulfate-sodium chloride electrolyte determined in our four years' research.\*

I congratulate Dr. Styri on his major conclusion; namely, that quenching removes all traces of contamination from the carbides in high-carbon steels. As you know, our work dealt only with the low-carbon steels and was not recommended for the tool steels that are interesting to Dr. Styri.

Dr. Styri's steels contain only such stable oxides as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , and, contrary to Dr. Kinzel's remarks, they contain insufficient quantities of either ferrous oxide or manganous oxide to be important. Hence, I do not understand why Dr. Styri expects to find manganese in his filtrates.

Unfortunately, Dr. Styri has not given any data concerning the hydrogen-ion concentrations and inclusion solubilities in each of his electrolytes. I trust that he has made such investigations, however, or he would hesitate to recommend the numerous solutions listed in Tables 2, 3 and 4. The data given in these tables are inadequate for the determination of solubilities of either sulfides or oxides in his solutions.

The fact that the volumetric residue analysis for sulfur is lower than the sulfur analysis of the steels would indicate to me that his solutions dissolve sulfides. Also, his Eschka sulfurs are higher than the total sulfur in the steel in two cases out of three. We were able to get excellent checks on all three types of sulfur determinations subsequent to electrolysis in the ferrous sulfate-sodium chloride solution.

Although no  $\text{MnO}$  or manganese silicates are present in Dr. Styri's steels, I am certain that they would be soluble in most of the "after treatments" listed in the fourth column of Table 3. Also, placing acid in the cathode chamber does not prevent its diffusion into the anode compartment. Is this not a reversion to the days of acid extractions?

Dr. Styri's suggestion that "X-ray analysis of inclusion residues should give an insight into their analyses" will not be borne out by the facts. More than a year ago we discovered that most of the inclusions resulting from deoxidation were amorphous and data from the X-ray and the petrographic microscope were practically useless. Inclusions originating from refractory erosion are, however, usually crystalline. Hence the X-ray may be useful in determining the sources of inclusions, but not their analyses.

Mr. Scott gives very little information concerning the characteristics of his magnesium iodide solution. Apparently no pH determinations have been made, and although this solution would probably be neutral at the start of electrolysis, its acidity would very likely increase rapidly during the electrolysis of a steel sample. Scott did attempt to make solubility determinations by placing crushed slags on top of an electrolyzing steel sample. However, he does not state whether his particle size approximated that of the average inclusion in steel, nor did he take into account in his analyses the inclusion content of his electrolyzing steel. Had he used electrolytic iron, this latter criticism would have been avoided.

Dr. Benedicks' interpretation (mentioned by Dr. Styri, p. 191) of our ferrous sulfate electrolyte is entirely erroneous.  $\text{MnO}$  is soluble in the freshly prepared sulfate-chloride electrolyte, which has a pH of 3. However, a review of my paper will reveal that the freshly prepared solution was not recommended. Dummy samples were to have been electrolyzed for at least three ampere-hours before the actual samples were to be connected to the circuit. After this time, and continuously through the 20 to 24-hr. electrolysis, this solution has an automatically controlled pH of 7 or neutrality, and  $\text{MnO}$  is only slightly soluble therein. To my knowledge this solution is the only one recommended to date that exhibits this very important characteristic.

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\* G. R. Fitterer and others: The Development of an Electrolytic Method for the Determination of Inclusions in Plain-Carbon Steels. U. S. Bur. Mines *Rept. of Investigations* 3205 (1933).

Dr. Benedicks' solution is neutral when freshly prepared, but before completion of a 20-hr. electrolysis has a pH of 5.3. This acidity is sufficient to dissolve  $\text{MnO}$ , the silicates and the sulfides. I would suggest that solubility studies be made at the pH of 5.3 rather than 7, so as more nearly to approximate working conditions.

C. BENEDICKS, Stockholm, Sweden (written discussion).—Having discussed the paper with Mr. H. Lofquist and Mr. R. Treje, I have pleasure in writing as follows. The results obtained by Dr. Styri are interesting in several respects. As regards the fundamental question, the proper choice of the electrolyte, but little information was obtained, as the checking factor available, the sulfur content of the residue, was found to be invariable, and to correspond to the actual analysis. The fact that in all cases the sulfide had not been attacked, in spite of the considerable acidity which apparently prevailed, is remarkable; it may be explained merely by the assumption of a comparatively high manganese content of the steels; unfortunately no Mn figures of the steels were given.

As was established in the paper by Treje and Benedicks,<sup>9</sup> the acidity due to the evolution of oxygen at the anode must be avoided; the only anions rationally to be used are consequently<sup>10</sup> Br and I. As actually seen from the decomposition tensions known, *viz*,

$\text{SO}_4$	Cl	$\text{O}^{11}$	Br	J
1 90	1 34	1 33	0 99	0 52

Br and J, respectively, are much more easily precipitated than oxygen, and are consequently the only rational ones.

If, in spite of this necessary theoretical requirement, Cl ions may be possible to use, as seems recommended by Dr. Styri, this must solely be ascribed to the fact that oxygen may receive a decomposition tension higher than that of Cl; *viz*, if the concentration of H ions is increased: the electrolysis will then possibly occur without evolution of oxygen. This method, however, is not to be recommended; the unfavorable influence of oxygen precipitation is actually that of increasing the acidity.

As for the conditions at the cathode, the following is to be said. Any increasing concentration of hydroxide ions—as caused by the precipitation of hydrogen gas—is to be avoided, in order to prevent the formation of hydroxide.

In the paper previously referred to (footnote 3), it was elucidated that the rational way to avoid this disadvantage was given by the following decomposition tensions: Cu, 0 33; H, 0 00; Fe, -0 43. Thus, any hydrogen evolution may be avoided by using a copper solution at the cathode; in order to avoid the diffusion of copper ions to the anode, a thick diaphragm must be used. Dr. Styri prevents the concentration of hydroxide ions at the cathode by the simple expedient of adding an acid to the cathode liquid. This, however, must cause a considerable diffusion of the acid through the cellulose cap used into the anode chamber, increasing its acidity.

If, in the case of a manganese-rich sulfide, the acid attack may be neglected, this is certainly not so in the case of steels containing (Mn, Fe) O or FeS inclusions. The prevention of such an attack must be considered to be the main difficulty in the electrolytic method. Should, in some special cases, a considerable acidity be permissible, there is scarcely any reason for using the more complicated electrolytic method, as an ordinary chemical dissolving in an acid liquid may serve. It should be

<sup>9</sup> Reference of footnote 3, 165.

<sup>10</sup> In a paper by F. W. Scott (reference of footnote 6) it was concluded from experiments—without any theoretical analysis—that an electrolyte containing magnesium iodide was much to be preferred to sulfates or chlorides.

<sup>11</sup> At a one-normal concentration of H ions.

kept in mind that the only true advantage of the electrolytic method consists in its offering a possibility of keeping a sensibly neutral liquid.

H. STYRI (written discussion).—We have not stated that the Bureau of Mines method cannot be used, but we found that the formation of basic sulfates made it difficult to wash the residues free for sulfates, so that we might easily get too high values for sulfur, in which we were particularly interested. We therefore tried other electrolytes that would cause no contamination with sulfates. We made a great number of tests on the solubility of powdered iron and manganese sulfides in different electrolytes and found that even 0.1N HCl at room temperature would dissolve 300-mesh powdered sulfide in 30 min. while 10 per cent acetic acid dissolved MnS in 15 min. but had little effect on FeS in 1 hr. Ten per cent iodine in alcohol at room temperature dissolves both sulfides.

With this easy attack of free sulfides in weak acid solutions, it was really surprising that we found so great a recovery of sulfur in the residue, because the solutions in the anode chamber, with, as far as we know, faithful following of the Bureau's recommended practice and with as much as 450 c.c. liquid in the anode chamber, increased in acidity by 0.1N, determined by titration in the presence of citric acid to prevent precipitation of hydroxides

We fail to understand how Dr. Fitterer has been able to obtain greater alkalinity in the anode chamber during electrolysis, unless diffusion from the alkaline cathode chamber has been sufficient to counterbalance the acidifying effect of gas evolution at the anode, or a precipitation of hydroxide on the electrode has masked his result. Gas evolution was found in all our solutions except Benedicks'. The migration of ions and less than 100 per cent efficiency must cause an increase in acidity in the anode chamber and increase in alkalinity in the cathode chamber and are probably more important than direct diffusion through the colloid membrane

The degree of change in acidity or alkalinity, of course, must depend on the volume of liquid in the two compartments. With a 2-in. collodion bag holding about 120 c.c., the acidity increased as much as 0.5N while a large anode compartment with 450 c.c. capacity only increased 0.1N.

The manganese in the residue was determined after the residue had been fused with Eschka mixture, but in checking the results it has been found that the determination of Mn in samples 4 and 5 were in error, owing to inefficient elimination of chloride during baking in preparation for titration by the bismuthate method. A determination of Mn in the residue by dissolving directly in HNO<sub>3</sub> and titrating with the bismuthate method gave the results shown in the accompanying table.

Electrolyte	Samples				
	1	2	3	4	5
Bureau of Mines . . . . .				0 25	0.033
10 per cent Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>7</sub> (anode) . . . . .				0 24	0 034
FeCl <sub>2</sub> . . . . .			0.029	0 20 (av. of 5)	0 034
Original Mn in steel, per cent . . . . .	0 28	1 10	0 94	0 45	0.32

The sulfur in the original samples 1, 4 and 5 was analyzed gravimetrically, which usually gives a few points lower than the volumetric analyses. The sulfur in 2 and 3 is that found by volumetric mill analyses.

The Eschka method was used on the residue in order to catch sulfur that might be dissolved in silicates or mixed with carbides and thus not so readily attacked by the acid in the volumetric analyses. The higher values of S than in the original found in experiment 152 are most probably due to contamination of the residue with basic sulfate.

For the experiments referred to in my discussion of Fitterer's paper, the Eschka method was used, for the reasons stated above, and not the volumetric method, as stated by Dr Fitterer [*Trans.* (1931) **95**, 215.].

We consider that the X-ray was very useful in showing the presence of carbides in residue from electrolyses of annealed samples and absence of carbides in residues of samples quenched from high temperatures. It is, of course, not to be expected that X-ray analyses would show anything on glassy slag particles, principally found in small ladle samples, but X-rays may be useful in identifying some of the crystalline slags. Hardly anyone who has seen slag in steel under the microscope would expect to find homogeneous slag, or only crystalline slag.

Dr Benedicks' discussion gives the only theoretically sound approach to a correct method of electrolysis, and it is most probable that future methods for determination of soluble oxides or sulfides must be developed along such lines. There is no particular difficulty in arranging diaphragms and solutions so that desired pH values may be maintained within definite limits, by a continuous check on acidity and necessary additions. In some tests we made, leaving the open top of the anode chamber submerging below the surface of the liquid for intermixing of anode and cathode liquid gave promising results, although some hydroxide was formed, which, however, would mostly float to the surface and could be shoved away when lifting the bag. The acidity in the anode chamber was reduced considerably and the recovery of manganese was a little greater than in the other method.

Future work must determine the limiting pH values that will prevent attack of sulfides and oxides and still prevent formation of hydroxides or basic salts.

It seems surprising that even such crude methods as described in the paper have given satisfactory recovery of sulfur in the steels used, which were selected at random among steels of particular interest to us. It is hoped that our efforts may induce other investigators to make comparative experiments.

# The Intermediate Phases of the Iron-tungsten System

By W. P. SYKES\* AND KENT R. VAN HORN,† CLEVELAND, OHIO

(Buffalo Meeting, October, 1932)

SINCE Honda and Murakami<sup>1</sup> in 1918 proposed their constitutional diagram of the carbon-free iron-tungsten system, considerable effort has been expended by several investigators in attempts to define more positively the structural features of the alloys. The existence of an intermediate phase corresponding to the formula  $\text{Fe}_3\text{W}_2$  (68.7 per cent W) was proposed from evidence of a purely metallographic nature by one of the present authors<sup>2</sup> in 1926. Since that time the identity of this phase has been confirmed by Arnfelt<sup>3</sup> and by Takeda,<sup>4</sup> both of whom employed X-ray methods as well as the microscope and the chemical analysis of isolated microconstituents. According to Arnfelt,  $\text{Fe}_3\text{W}_2$ , as crystallized from the iron-rich melts at a temperature above  $1450^\circ\text{C}$ ., contains by analysis 68.7 per cent W. The lattice of this phase is characterized by trigonal symmetry.

Arnfelt, moreover, proposed a second intermediate phase formed at some temperature between  $1450^\circ$  and  $1000^\circ\text{C}$ . by a peritectoid reaction involving  $\text{Fe}_3\text{W}_2$  and the iron-rich solid solution. A melt containing 25 per cent W was cooled to  $1000^\circ\text{C}$ . and heated for 100 hr. The precipitated tungsten-rich constituent was separated and found by analysis to contain 62.6 per cent W. This composition agrees closely with that represented by the formula  $\text{Fe}_2\text{W}$  (62.2 per cent W). Diffraction patterns from the concentrated precipitate showed a hexagonal unit cell.

Takeda confirmed the data of Arnfelt regarding  $\text{Fe}_3\text{W}_2$  but was unable to detect Arnfelt's second intermediate phase. While Takeda failed to describe in detail the treatments employed, he stated that in alloys containing 40 per cent W which were quenched after heating at various temperatures between  $1200^\circ$  and  $1450^\circ\text{C}$ . no evidence of the second phase ( $\text{Fe}_2\text{W}$ ) was observed either in the microstructure or in the diffraction patterns of isolated residues. He therefore considered the existence of this low-temperature hexagonal compound as disproved.

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<sup>1</sup> K. Honda and K. Murakami: *Sci. Repts. Tohoku Imp. Univ.* (1918) 6, 264.

<sup>2</sup> W. P. Sykes: *Trans. A. I. M. E.* (1926) 73, 968.

<sup>3</sup> H. Arnfelt: *Jnl. Iron and Steel Inst., Carnegie Schol. Mem.* (1928) 17.

<sup>4</sup> S. Takeda: *Tech. Repts. Tohoku Imp. Univ.* (1930) 9.

Takeda, in his turn, introduced an additional phase in the range of composition between 80 and 90 per cent W and stable above 1550° C. It was inferred to be peritectically formed by a reaction between the tungsten-rich solid solution and the iron-rich melt. Evidence for the existence of this phase (designated as X) is very meager, as admitted by Takeda, and was recognized solely by certain coloring effects observed in the microstructure of tungsten-rich alloys which had been partially melted, after the polished surface had been etched with alkaline  $K_2FeCN_6$ .

In view of the apparent disagreement concerning the low-temperature intermediate compound, the present authors decided to explore the ranges of composition and temperature involving the formation of this phase.

The iron used in this investigation was in the form of powder reduced in hydrogen from precipitated iron oxalate. The carbon content was less than 0.01 per cent. The purity of the tungsten powder was at least 99.8 per cent and represents the quality used for lamp filaments. Alloys were prepared by sintering pressed powders in hydrogen or by melting the pressed metals in alundum boats, likewise in an atmosphere of hydrogen. The history of each specimen is recorded in Table 1.

All of the extended heat treatments described were performed in a tungsten-wound resistor furnace, operating in a hydrogen atmosphere. A reducing valve in the hydrogen supply line maintained a nearly constant gas flow through the furnace. The furnace after having attained any desired temperature between 1000° and 1600° C. could be held at this temperature with a variation of not more than  $\pm 1$  per cent over a period of several days by means of a voltage regulator operated by automatic control.

The tungsten-rich constituents in the 30 and 45 per cent tungsten melts were isolated by electrolytic solution. The alloys, after heat treatment, were immersed as anodes in a 10 per cent HCl solution. Electrolysis at a current density of 0.15 to 0.25 amp. per sq. cm. dissolved the iron-rich solid solution while the tungsten-rich particles were collected in a receptacle placed beneath the anode. A considerable quantity of tungsten oxide formed during the operation and was dissolved by subsequently treating the residue with an ammonia solution. Following this treatment the concentrate was washed with water and then with the 10 per cent HCl solution. After a few similar cycles the excess iron and tungsten were eliminated, leaving the white lustrous crystals of the intermediate phase, which was then used for chemical and diffraction analysis.

#### X-RAY ANALYSIS

##### *Preparation of Samples and Diffraction Methods*

A number of diffraction patterns were made of specimens prepared by powdering fused alloys which had received extended heat treatments

at various temperatures. Binary alloys containing from 55 to 90 per cent W were brittle and could be pulverized in a steel mortar and pestle to pass a 300-mesh screen. It was also desirable to isolate the constituents in the more dilute and less brittle iron-base melts (30 to 45 per cent W) in order to procure intense X-ray reflections. The constituents were obtained in concentrated form as a residue that could be powdered easily, from the solution of the alloy in which they occurred. The sample for analysis was placed in one part of a Pyrex glass capillary tube, 1 mm. outside diameter, then a separating cotton plug was inserted and a sodium chloride standard was placed in the other part. The capillary tube was sealed at the extremities and centered on a General Electric cassette containing a zirconium oxide filter.

Photograms were also obtained by the Wedge method of small blocks which had been pressed and sintered at the desired temperatures. The inaccuracies due to specimen size and variation in penetration are avoided by this procedure, which permits the further advantage of examining block samples.

Powder and reflection patterns were produced on a General Electric X-ray apparatus equipped with a molybdenum target tube, operating at 30,000 volts and 20 milliamperes. The exposure periods with Eastman Diaphax films were from 48 to 72 hr., dependent on the tungsten content. In measuring the position of the reflections, corrections were made for any dimensional changes in the film by reference to a sodium chloride or Armco ingot iron pattern, which was recorded on each photogram. The various lines were rated as to intensity, five degrees of intensity being recognized.

### *Discussion of Results*

A number of fused or sintered binary alloys containing from 30 to 90 per cent W, which had received various heat treatments designed to approximate equilibrium conditions, have been investigated. The photograms revealed two intermediate phases in addition to alpha iron and metallic tungsten. The patterns of the two intermediate phases were somewhat similar because of the coincidence of a number of reflections but, on careful examination, could easily be differentiated (Fig. 1). One of the compounds, which will be designated as the low-temperature phase,  $\epsilon$ , occurred in all mixtures (55 to 70 per cent W) pressed and sintered at 1000° to 1025° C. or in melts containing 30 per cent W which had been heated for extended periods at 1000° to 1030° C. The other compound, which will be referred to as the high-temperature phase,  $\beta$ , was present in melts of 30 per cent W heat-treated at or above 1050° C. and of 45 per cent W heated at or above 1000° C.; also in higher tungsten concentrations (55 to 90 per cent W) sintered at 1450° C. or subsequently heated for 125 hr. at 1000° C. The composition of the alloys, methods

of preparation and heat treatments which produced the low-temperature compound  $\epsilon$  are listed in Table 1, while Table 2 gives the conditions required for the formation of the high-temperature phase  $\beta$ . A number of the melts described at the beginning of Table 2 were slowly cooled from the fusion temperature to each preliminary homogenizing temperature before reaching that of the final heat treatment. Unless intermediate quenching and reheating is noted in the table, this procedure was followed in all cases. All specimens listed in Tables 1 and 2 were quenched from the final heating or sintering temperatures. It is significant that there were no photograms in which the patterns of the two intermetallic phases  $\beta$  and  $\epsilon$ , were superimposed.

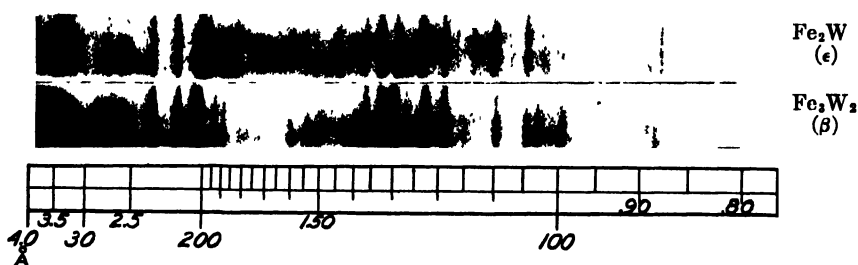


FIG. 1.—DIFFRACTION PATTERN OF THE TWO INTERMEDIATE PHASES.

Melts containing 30 and 45 per cent W were slowly cooled to each preliminary homogenizing temperature and finally heated for 100 hr. at either  $1350^{\circ}\text{C.} \pm 10^{\circ}\text{C.}$  or  $1050^{\circ}\text{C.} \pm 10^{\circ}\text{C.}$  (samples Fe-30W-X-2 and X-3, Fe-45W-X-3 and X-4). The constituents were electrolytically isolated, pulverized, examined by the X-ray and found to consist of the high-temperature phase  $\beta$ . It was thought that distortion, causing an unstable condition, might be introduced by the cold work incident to the preparation of the powdered specimens. Therefore the powders were reheated for 50 hr. at  $1350^{\circ}$  or  $1050^{\circ}\text{C.}$ , exposed and reproduced the high-temperature  $\beta$  configuration. This experiment was performed to check the method although it was thought that the mechanical disturbance involved in filing might tend to effect equilibrium which could not be realized by long heat treatments.

Constituents separated from the 30 per cent W melt which had been heated from 25 to 400 hr.<sup>5</sup> at  $1000^{\circ}$  to  $1030^{\circ}\text{C.}$  (samples Fe-30W-X-1, Fe-30W-X-4 to X-8) revealed the pattern of the low-temperature compound  $\epsilon$ . It seemed likely that this phase might have formed directly by precipitation from the iron-rich solid solution at  $1000^{\circ}$  to  $1030^{\circ}\text{C.}$  in the cases just described. Consequently, Fe-30W-X-9 was treated

<sup>5</sup> Fe-30W-X-1 was treated at  $1000^{\circ}\text{C.}$  for 5 hr., which was thought to be insufficient time to complete the sluggish transformation.



first at 1100° C. to precipitate a considerable quantity of the  $\beta$  which it was thought might be converted into the  $\epsilon$  form by subsequent heating at 1000° to 1030° C. As noted in Table 1, this proved to be the case. It would appear, therefore, that the peritectoid reaction  $\alpha + \beta \rightleftharpoons \epsilon$  occurs between the temperatures 1030° and 1050° C. in alloys of 30 per cent W content.

It was decided to determine whether the transition range could be defined by similar heat treatments of the 45 per cent W melt. Specimens (Fe-45W-X-6 and X-7) which had been homogenized for various periods at higher temperatures were heated for 25 and 50 hr.<sup>6</sup> at 1000° C. The photograms of the concentrated constituent showed only the high-temperature phase. This result can be explained either by incomplete equilibrium or that the low-temperature  $\epsilon$  region does not extend to 45 per cent W, which seems very improbable.<sup>7</sup>

Slow cooling of the samples between extended homogenizing treatments at a number of temperatures and exceptionally long heating at the final temperature 1000° to 1025° C. did not induce in the 45 per cent W specimens the peritectoid reaction which the 30 per cent W melts indicated to occur about 1030° to 1050° C. Also, further experiments with alloys containing 55 to 75 per cent W which had been sintered and heat-treated 75 hr. at 1450° to 1500° C. or subsequently heated at 1000° to 1025° C. for 125 hr., revealed only the high-temperature compound  $\beta$  and in some cases the elements iron or tungsten. The failure to develop the low-temperature  $\epsilon$  phase in the heat-treated higher tungsten (45 to 75 per cent W) alloys may be attributed to the massive structure of the  $\beta$  constituent. Large primary crystals would probably grow during solidification and additional  $\beta$  is precipitated from solid solution during the slow cooling to and heating at the homogenizing treatments above 1050° C. The precipitate from the iron-rich solid solution may collect and coalesce on the primary particles, producing massive  $\beta$  areas. The reaction in the solid to obtain  $\epsilon$  at the expense of  $\beta$  at or below 1050° C. would probably form sheaths or envelopes of  $\epsilon$  around the pre-existing masses of  $\beta$ . The large tungsten atoms would then have to diffuse outward from the center and the smaller iron atoms would have to migrate inward from the surrounding  $\alpha$  iron solid solution in order to obtain equilibrium. The speed of this reaction would rapidly decrease as the  $\epsilon$  sheath is developed and particularly when the  $\beta$  regions are massive. This hypothesis is strengthened by the microstructure of the

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<sup>6</sup> This alloy was heated only 50 hr. at 1000° C. and it is possible, in view of the data later obtained from sintered material, that longer heating might have resulted in the formation of the low-temperature  $\epsilon$ .

<sup>7</sup> Chemical analysis of the isolated  $\epsilon$  phase present in the heat-treated 30 per cent W melt gave approximately the composition represented by the formula Fe,W.

45 per cent W melt after prolonged heating in range of 1200° C. which revealed large primary  $\beta$  crystals about which an abundance of secondary precipitate had formed.

The peritectoid reaction proceeds more readily on heating a lower tungsten alloy (30 per cent W) for 25 or more hours at 1000° to 1030° C. because the composition-temperature conditions are less conducive to the previous formation of large areas of the high-temperature compound. The microscope did not show any primary  $\beta$  regions in the 30 per cent W samples. The  $\beta$  particles precipitated from the solid solution are relatively small in comparison with the areas of the same phase in the 45 per cent W alloy after slow cooling to 1100° C.

It was thought that if these observations were correct, it would be possible to produce the low-temperature phase  $\epsilon$  directly by pressing and sintering higher tungsten mixtures at or below the supposed peritectoid temperature 1030° to 1050° C. This method of preparation would eliminate the formation of large primary  $\beta$  crystals. Specimens containing 55 per cent W were pressed and sintered for 5, 25 and 75 hr. at 1000° to 1025° C. Reflection photograms of the material sintered for 5 and 25 hr. revealed strong  $\alpha$  iron and tungsten lines and medium reflections of the low-temperature phase  $\epsilon$ . The sample sintered for 75 hr. showed weak  $\alpha$  lines and intense  $\epsilon$  reflections. The alloy was also sintered for 5 and 25 hr. at 1075° to 1100° C. and the resulting X-ray films revealed the presence of the low-temperature and high-temperature compounds, respectively. This suggests that the reaction proceeds from  $\text{Fe} + \text{W} \rightarrow \epsilon \rightarrow \beta$ . Some estimation of the reaction velocity can be gained from the sintering times. Alloys containing 60, 65 and 70 per cent W were sintered for 150 hr. at  $1000^\circ \pm 10^\circ$  C. and the diffraction analysis showed the low-temperature  $\epsilon$  to be the major constituent. Specimens of the same compositions sintered and heat-treated at 1450° to 1500° C. and subsequently heated for 125 hr. at 1000° to 1025° C., consisted of the  $\beta$  phase as previously described. This result seems to indicate that  $\beta$  once formed by sintering in the composition range 55 to 75 per cent W is extremely difficult to convert to  $\epsilon$  by heating at a lower temperature. It should be noted that patterns of the two compounds  $\beta$  and  $\epsilon$  never occurred on the same film.

According to Takeda, the X phase which he proposes should occur in the range of composition between 80 and 90 per cent W at a temperature immediately below the solidus. Alloys containing 80, 85 and 90 per cent W were prepared by mixing the metal powders, pressing and sintering, in order to obtain additional evidence, if possible, concerning such a phase. The sintering schedule was as follows: 1425° to 1500° C. for 25 hr. and 1600° to 1625° C. for 50 hr. The alloys were cooled quickly after this treatment and sections removed for microscopic examination. Specimens of each composition were then placed together in a furnace

at 1630° C. and the temperature raised<sup>s</sup> in 30 min. to 1650 ± 6° C. After holding for 10 min., the samples were cooled to room temperature in about 1 min. The metallographic examination showed positive evidence of liquid formation in all three compositions. The significance of this fact will be discussed later in the section on microstructures. The alloys were also analyzed by diffraction methods and found to consist only of high-temperature Fe<sub>3</sub>W<sub>2</sub> and tungsten.

TABLE 1.—*Method of Preparation and Treatment of Iron-tungsten Alloys Containing the Low-temperature (Fe<sub>2</sub>W) Phase as Determined by Diffraction Analysis*

Specimen	Tungsten, Per Cent	Type of Material	Preliminary Homogenizing or Sintering Treatment	Final Heating or Sintering Temperature, Deg C	Time at Temperature, Hr	Additional Phases Present
Fe-30W-X-1	30	Melt and precipitate isolated	Solidified at 1500° C, quenched and reheated	1000 ± 15	50	
Fe-30W-X-4	30	Melt and precipitate isolated	Fused at 1500° C, quenched and reheated	1020 ± 15	25	
Fe-30W-X-5	30	Melt and precipitate isolated	Fused at 1500° C, quenched and reheated	1020 ± 15	50	
Fe-30W-X-6	30	Melt and precipitate isolated	Fused at 1500° C, quenched and reheated	1020 ± 15	100	
Fe-30W-X-7	30	Melt and precipitate isolated	Fused at 1500° C, quenched and reheated	1020 ± 15	200	
Fe-30W-X-8	30	Melt and precipitate isolated	Fused at 1500° C, quenched and reheated	1020 ± 15	400	
Fe-30W-X-9	30	Melt and precipitate isolated	Fused at 1650° C, cooled to 1600° in 10 min, cooled to 1500° in 10 min, quenched, reheated and annealed at 1300° and 1200° for 25 hr. and 1075 to 1100° for 50 hr	1000 to 1025	100	
Fe-45-W-55-1	55	Pressed and sintered		1000 to 1025	5	Considerable W and Fe
Fe-45-W55-2	55	Pressed and sintered		1000 to 1025	25	Considerable W and Fe
Fe-45-W55-2a	55	Pressed and sintered		1000 to 1025	75	A little Fe
Fe-45-W-55-3	55	Pressed and sintered		1075 to 1100	5	Considerable Fe
Fe-60W-X-3	60	Pressed and sintered		1000 ± 15	150	Considerable Fe
Fe-65W-X-3	65	Pressed and sintered		1000 ± 15	150	Considerable W and Fe
Fe-70W-X-3	70	Pressed and sintered		1000 ± 15	150	Considerable W

<sup>s</sup> The temperature was determined with an optical pyrometer sighted upon an alundum target immediately behind the alloy blocks.

TABLE 2.—*Method of Preparation and Treatment of Iron-tungsten Alloys Containing the High-temperature ( $Fe_3W_2$ ) Phase as Determined by Diffraction Analysis*

Specimen No	Tungsten, Per Cent	Type of Material	Preliminary Homogenising or Sintering Treatment	Final Heating or Sintering Temperature, Deg C.	Time at Temperature, Hr	Additional Phases Present
Fe-30W-X-2	30	Melt and precipitate isolated	Solidified at 1520° C, cooled to and then annealed at both 1450° and 1400° for 50 hr	1350	100	
Fe-30W-X-3	30	Melt and precipitate isolated	Same as Fe-30W-X-2 + 100 hr anneal at 1350° and cooling to and then heating at 1300°, 1200°, 1150° and 1100° C each for 50 hr	1050	100	
Fe-30W-X-10	30	Melt and precipitate isolated	Solidified at 1500° C., cooled to 1100° in 30 min and annealed.	1100 ± 10	25	
Fe-30W-X-11	30	Melt and precipitate isolated	Solidified at 1500° C, cooled to 1100° in 30 min, quenched and reheated	1000 ± 10	5	
Fe-45W-X-1	45	Melt and precipitate isolated	Solidified at 1600° C, cooled to 1520° in 25 min and quenched.	1520		
Fe-45W-X-3	45	Melt and precipitate isolated	Fused at 1700° C, cooled to 1600° in 5 min, cooled to 1500° in 30 min, cooled to and then heated at both 1400° and 1450° for 50 hr	1350	100	
Fe-45W-X-4	45	Melt and precipitate isolated	Melted at 1700° C, cooled to 1640° in 5 min, cooled to 1500° in 20 min and quenched Reheated and annealed at 1450° and 1400° each for 50 hr, 1350° for 100 hr, 1300°, 1200°, 1150° and 1100° for 50 hr.	1050	100	
Fe-45W-X-5	45	Melt and precipitate isolated	Fused at 1650° C, cooled to 1600° in 10 min, cooled to 1500° in 10 min, quenched, reheated and annealed at 1300° and 1200° for 25 hr	1075 to 1100	50	
Fe-45W-X-6	45	Melt and precipitate isolated	Same as Fe-45W-X-5 + cooling to 1000° to 1025° C.	1000 to 1025	25	
Fe-45W-X-7	45	Melt and precipitate isolated	Same as Fe-45W-X-5 + cooling to 1000° to 1025° C	1000 to 1025	50	
Fe-45-W55-4	55	Pressed and sintered		1075 to 1100	25	Considerable Fe
Fe-55W-X 1	55	Pressed and sintered		1450 to 1500	75	
Fe-55W-X-2	55	Pressed and sintered	Sintered at 1450° to 1500° C for 75 hr., quenched and reheated (part of Fe-55W-X-1)	1000 to 1025	125	Possibly Fe
Fe-60W-X-1	60	Pressed and sintered		1450 to 1500	75	
Fe-60W-X-2	60	Pressed and sintered	Sintered at 1450° to 1500° C for 75 hr, quenched and reheated (part of Fe-60W-X-1)	1000 to 1025	125	
Fe-62W-X-1	62	Pressed and sintered		1450 to 1500	75	Possibly Fe

TABLE 2.—(Continued)

Specimen No	Tungsten, Per Cent	Type of Material	Preliminary Homogenising or Sintering Treatment	Final Heating or Sintering Temperature, Deg C	Time at Temperature, Hr	Additional Phases Present
Fe-62W-X-2	62	Pressed and sintered	Sintered at 1450° to 1500° C for 75 hr., quenched and reheated (part of Fe-62W-X-1)	1000 to 1025	125	
Fe-65W-X-1	65	Pressed and sintered		1450 to 1500	75	
Fe-65W-X-2	65	Pressed and sintered	Sintered at 1450° to 1500° C. for 75 hr., quenched and reheated (part of Fe-65W-X-1)	1000 to 1025	125	
Fe-70W-X-1	70	Pressed and sintered	Sintered at 1450° to 1500° C for 75 hr. and heated	1800 to 1625	50	
Fe-70W-X-2	70	Pressed and sintered	Sintered at 1450° to 1500° C for 75 hr, heated 50 hr at 1800° to 1625°, quenched and reheated (part of Fe-70W-X-1)	1000 to 1025	125	
Fe-75W-X-1	75	Pressed and sintered	Sintered at 1450° to 1500° C for 75 hr and heated	1800 to 1625	50	Possibly W
Fe-75W-X-2	75	Pressed and sintered	Sintered at 1450° to 1500° C for 75 hr, heated 50 hr at 1800° to 1625°, quenched and reheated (part of Fe-75W-X-1).	1000 to 1025	125	
Fe-80W-1	80	Pressed and sintered	Sintered at 1425° to 1500° C for 25 hr, heated 1800° to 1625° C for 50 hr., quenched and reheated	1650 ± 6	10 min	
Fe-85W-1	85	Pressed and sintered	Sintered at 1425° to 1500° C for 25 hr, heated 1800° to 1625° C for 50 hr, quenched and reheated	1650 ± 6	10 min	Considerable W
Fe-90W-1	90	Pressed and sintered	Sintered at 1425° to 1500° C for 25 hr, heated 1800° to 1625° C for 50 hr, quenched and reheated	1650 ± 6	10 min	Considerable W

## IDENTIFICATION OF INTERMEDIATE IRON-TUNGSTEN PHASES

The photograms of the various iron-tungsten alloys confirm the previous conclusions of Chartkoff and Sykes,<sup>9</sup> Arnfelt, and others, that solute tungsten atoms appreciably increase the  $\alpha$  iron unit cell dimensions. Calculations have shown the solution to be of the simple substitutional type. The X-ray films of Fe-70W-X-3, Fe-85W-1 and Fe-90W-1 revealed the presence of excess tungsten, which registered a definite lattice expansion, checking the observation of Chartkoff and Sykes that the solution of iron in tungsten is of the interstitial type.

The interplanar spacings computed from the patterns of alloys containing the  $\beta$  and  $\epsilon$  phases agreed well with those reported by Arnfelt. A definite lattice expansion was observed in the  $\beta$  phase as the tungsten content of the alloy increased from 45 to 90 per cent, especially after heating at a temperature near the solidus. In the  $\epsilon$  phase a similar expansion was evident between the composition limits of 30 and 70 per cent tungsten.

<sup>9</sup> E. P. Chartkoff and W. P. Sykes: *Trans. A.I.M.E.* (1930) **89**, 566.

It appears likely that true equilibrium as defined by constant interplanar spacings in these intermediate phases can be attained only by heating for periods much longer than those used in this investigation. Consequently no quantitative conclusions are warranted as to the effect of composition upon the lattice dimensions.

Chemical analyses of  $\beta$  and  $\epsilon$  were made of isolated residues and are summarized in Table 3, together with those of Arnfelt and Takeda.

TABLE 3.—*Chemical Analyses of Isolated Residues*

Specimen No	Phase <sup>a</sup>	Tungsten, Per Cent
Fe-30W-X-9	$\epsilon$	62.9
Fe-30W-X-10	$\beta$	69.2
Fe-45W-X-5	$\beta$	68.9
By Arnfelt.	$\epsilon$	62.6
By Arnfelt	$\beta$	68.7
By Takeda	$\beta$	Max. 68.4 Min. 66.0

<sup>a</sup> Theoretical tungsten content of phases represented by the formula

$\text{Fe}_2\text{W} = 62.2 \text{ per cent.}$

$\text{Fe}_4\text{W}_2 = 68.7 \text{ per cent.}$

### MICROSTRUCTURES

It appeared desirable to detect, if possible, any positive change in microstructure which might result from the peritectoid reaction between the iron-rich solid solution  $\alpha$  and the high-temperature intermediate phase  $\beta$ . The evidence of this reaction might be expected to occur in the microstructure as a sheath inclosing a pre-existing area of  $\beta$  which had been precipitated from the  $\alpha$  solid solution above 1100° C. Consequently, a 30 per cent W alloy was examined after slow cooling from 1500° to 1100° C. and holding at the latter temperature for 25 hr. The resulting structure is illustrated in Fig. 2 which shows well defined  $\beta$  crystals distributed through the  $\alpha$  solid solution.

After this specimen was reheated at 1000° C. for 5 hr. and etched in the same manner, the appearance was considerably altered (Fig. 3). Border zones of some width now surround the  $\beta$  areas. These envelopes are actually dissolved as well as tinted with an oxide film by the etching reagents.<sup>10</sup> In fact, some of the smaller particles seemingly have been removed to some depth below the polished surface.

<sup>10</sup> A variety of etching reagents and cycles were tested in the attempt to develop a procedure for positively distinguishing between the high-temperature and low-temperature intermediate phases in the structure of the 30 per cent W alloy. The following procedure proved to be the most satisfactory: a preliminary electrolytic etch (5 sec.) in a solution of 10 per cent HCl (1 part) +  $\text{H}_2\text{O}_2$  (1 part) using a current

If greater susceptibility to the etchant attack is characteristic of  $\epsilon$ , it should be observed in this phase precipitated directly from the solid solution at 1000° C. The specimen prepared for this experiment was

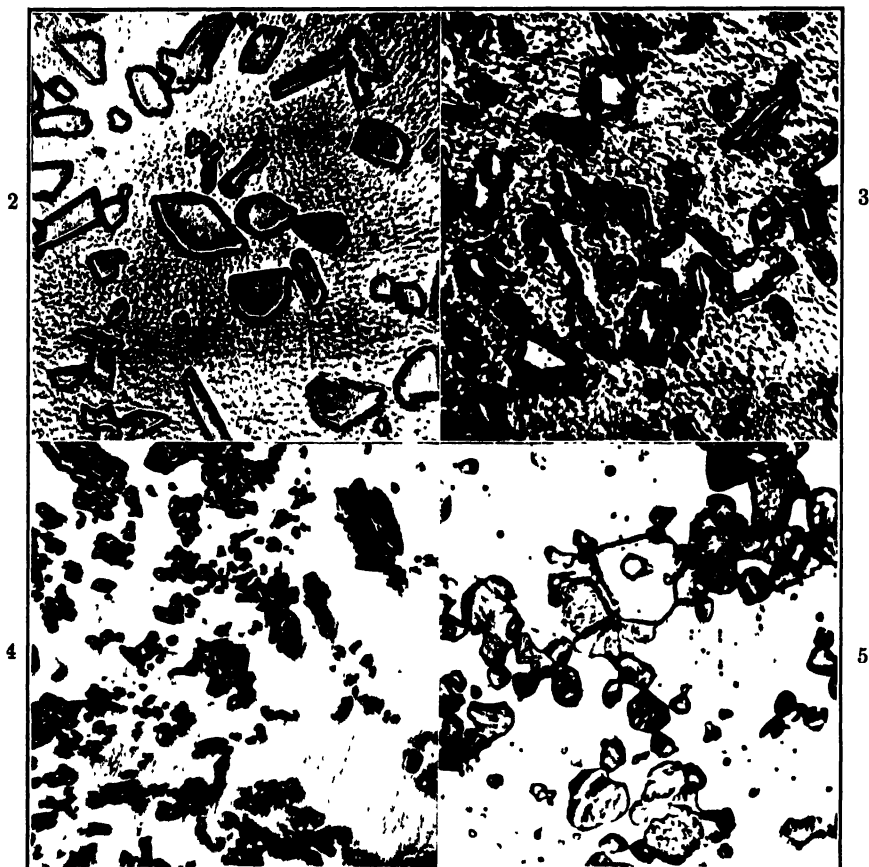


FIG. 2.—IRON, 70 PER CENT; TUNGSTEN 30 PER CENT. COOLED FROM 1500° TO 1100° C. IN 30 MIN. HELD AT 1100° C.  $\pm$  15° C. FOR 25 HR. QUENCHED.  $\times$  1000.

FIG. 3.—SAME COMPOSITION AND TREATMENT AS FIG. 2. REHEATED AT 1000°  $\pm$  15° C. FOR 100 HR.  $\times$  1000.

FIG. 4.—IRON, 70 PER CENT; TUNGSTEN, 30 PER CENT. QUENCHED FROM 1500° C. REHEATED AT 1000°  $\pm$  15° C. FOR 100 HR.  $\times$  1000.

FIG. 5.—TUNGSTEN, 80 PER CENT; IRON, 20 PER CENT. SINTERED 1450° TO 1500° C. FOR 25 HR.; 1600° TO 1625° C. FOR 50 HR. COOLED TO BLACK IN 1 MIN. ETCHED KOH +  $K_2FeCN_6$ .  $\times$  500.

quenched from 1500° C. and then reheated at 1000° C. for 100 hr. The microstructure, after etching in the same manner as the two preceding cases, is shown in Fig. 4. The precipitate appears to respond to the etch

density of about 0.1 amp. per sq. cm. outlines the constituents. The specimen is subsequently immersed for 10 min. in a solution consisting of  $H_2O_2$  (1 part) + 10 per cent KOH (2 parts).

in the same manner as the border zones in Fig. 3. However, the etching characteristics of the constituents are not sufficiently positive to establish the existence of the two distinct intermediate phases. The diffraction

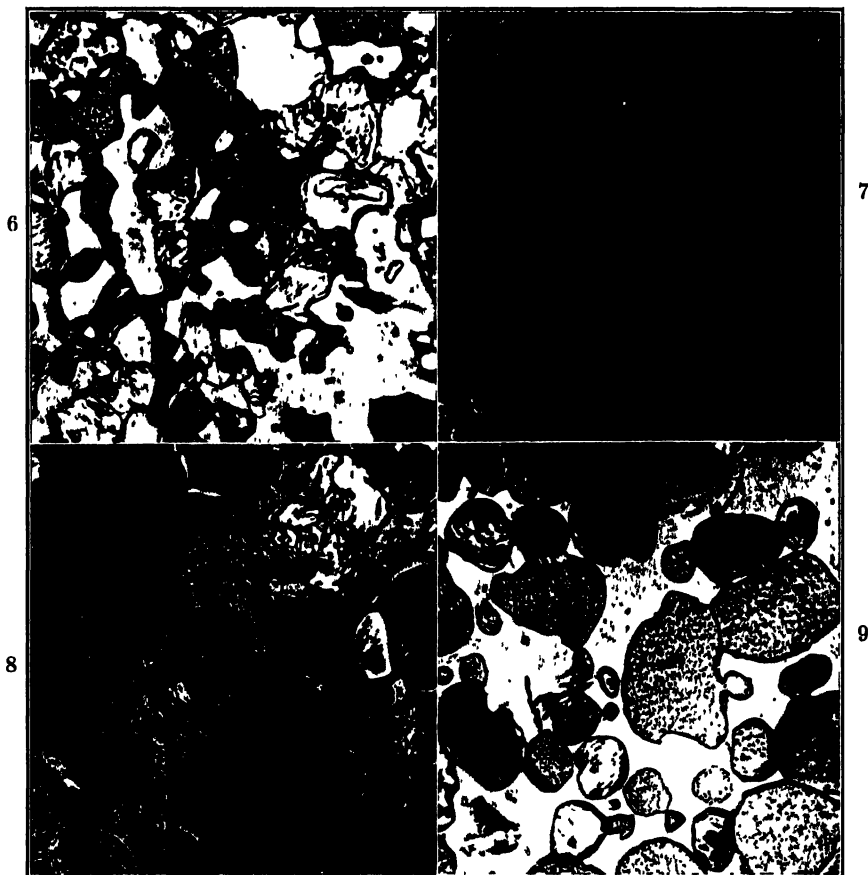


FIG. 6.—TUNGSTEN, 90 PER CENT; IRON, 10 PER CENT. SINTERED 1450° TO 1500° C. FOR 25 HR.; 1600° TO 1625° C. FOR 50 HR. COOLED TO BLACK IN 1 MIN. ETCHED KOH +  $K_2FeCN_6$ .  $\times 500$ .

FIG. 7.—TUNGSTEN, 90 PER CENT; IRON, 10 PER CENT. TREATED AS FIG. 6. SUBSEQUENTLY HEATED AT 1650° C.  $\pm 6^\circ$  C. FOR 5 MIN. AND COOLED TO BLACK IN 1 MIN. ETCHED 10 PER CENT NITAL.  $\times 500$ .

FIG. 8.—SAME AS FIG. 7. ETCHED KOH +  $K_2FeCN_6$ .  $\times 500$ .

FIG. 9.—TUNGSTEN, 90 PER CENT; IRON, 10 PER CENT. TREATED AS FIG. 6. THEN HEATED TO 1670° C. COOLED TO 1500° C. IN 90 MIN. HELD 1500° C. FOR 15 HR. ETCHED KOH +  $K_2FeCN_6$ .  $\times 500$ .

patterns definitely identified the  $\epsilon$  and  $\beta$  and thus showed the difference in microstructures to be significant.

At the risk of repetition it seems advisable to include a few photomicrographs typical of the composition range from 80 to 90 per cent W in which Takeda's X phase supposedly occurs. The preliminary treat-



ment of three alloys containing 80, 85 and 90 per cent W has been described previously. After sintering at a maximum temperature of  $1625^{\circ}\text{C}$ ., the microstructures consist of two well defined constituents. A scattering of the tungsten-rich solid solution appears in a  $\beta$  groundmass in Fig. 5.

The microsections of the high-tungsten (80 to 90 per cent W) samples were etched in a solution of equal parts of 10 per cent KOH and 10 per cent  $\text{K}_3\text{FeCN}_6$  for 5 min., unless otherwise noted. This etchant, which is similar to that used by Takeda, attacks the tungsten-rich solid solution but has no effect upon the surrounding  $\beta$  phase. The particles of tungsten-rich solid solution are appreciably roughened and coated by an oxide film. The film varies in thickness quite arbitrarily from one location to another. Even throughout any particular area, a wide variety of colors may be observed. The tungsten-rich solid solution, as identified by this etch, increases with the addition of tungsten, until it occupies the entire field at a composition of 98.7 to 98.9 per cent W. The relative quantities of the two phases in a 90 per cent W alloy quenched from  $1625^{\circ}\text{C}$ . are illustrated in Fig. 6, in which the irregular tinting of the tungsten-rich solid solution is strikingly evident.

It is possible to obtain iron-rich liquid by heating these three compositions to  $1650 \pm 6^{\circ}\text{C}$ . The iron-rich spots, inclosed by the phase, are readily attacked by a 10 per cent nital solution as shown in Fig. 7. The tungsten-rich solid solution has assumed a more nearly circular outline characteristic of a solid phase involved in a peritectic reaction. Since these specimens showed no liquid after heating to  $1625^{\circ}\text{C}$ ., the temperature of the peritectic reaction is approximately  $1640^{\circ}\text{C}$ ., the value originally<sup>11</sup> assigned throughout the range of composition between 60 and 98.8 per cent W.

It is of interest, moreover, to note that liquid had formed in all of the three alloys, 80, 85 and 90 per cent W, after simultaneous heating at  $1650^{\circ}\text{C}$ ., which indicates that there is not a measurable rise in the solidus temperature throughout this concentration range as would be required for the existence of the additional solid phase X. On the basis of available data, therefore, it would seem that the peritectic horizontal extends throughout this range of composition at about  $1640^{\circ}\text{C}$ . and is represented by *HLN* in the diagram (Fig. 10).

The tungsten-rich solid solution islands in a 90 per cent W sample quickly cooled from  $1650^{\circ}\text{C}$ . are sharply outlined, roughened and tinted, by applying the alkaline  $\text{K}_3\text{FeCN}_6$  etch. The variation in color is again quite irregular throughout the field (Fig. 8). Some of the solid solution areas, as observed by Takeda, exhibit darkened borders. However, careful inspection of this type of structure, especially with oblique

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<sup>11</sup> Reference of footnote 2.

illumination and on deeply etched specimens, proved the darkened borders to be shadows due to difference in elevations of the microconstituents.

The X phase was presumed by Takeda to decompose upon cooling through some temperature above  $1500^{\circ}\text{C}$ ., resulting in a eutectoid of tungsten-rich solid solution and  $\beta$ . In order to disclose such a possibility, the three compositions previously described were sintered and then heated at  $1670^{\circ}\text{C}$ . for 10 min. to form a considerable quantity of liquid. The alloys were subsequently cooled from  $1670^{\circ}$  to  $1600^{\circ}\text{C}$ . in 30 min.,

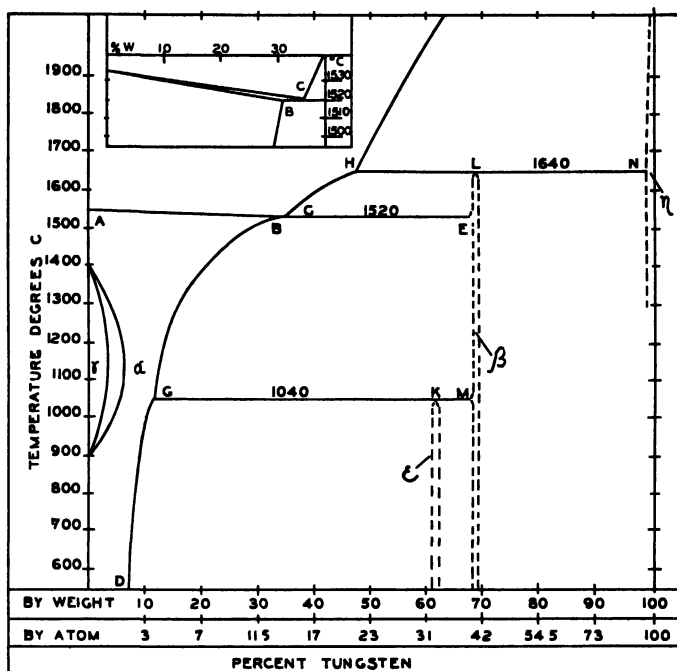


FIG. 10 —CONSTITUTIONAL DIAGRAM OF THE IRON-TUNGSTEN SYSTEM

from  $1600^{\circ}$  to  $1500^{\circ}\text{C}$ . in 1 hr. and finally held at  $1500 \pm 15^{\circ}\text{C}$ . for 15 hr. The resulting structure is illustrated in Fig. 9, which is typical of all three compositions, and no indication of a eutectoid transformation can be detected.

### SUMMARY

From the data previously published and that presented in the preceding pages, the constitutional diagram of the iron-tungsten system (Fig. 10) has been constructed. It is felt that this embodies all the data thus far available.

Among the features which perhaps require comment is the eutectic at about 33 per cent W. The eutectic composition was placed at 49

per cent W because of an incorrect interpretation of microstructure by one of the authors in an earlier paper.<sup>12</sup> Soon after publication, this error was noticed and has since been corrected by both Arnfelt and Takeda.

The temperature of the peritectoid reaction ( $\alpha + \beta \rightleftharpoons \epsilon$ ) appears to be about 1040° C. as represented by the line *GKM*. Takeda failed to observe this reaction because no heat treatments were performed below 1200° C.

It has not been possible to determine exactly the homogeneity ranges of the intermediate phases because of the difficulty in forming the compounds and attaining equilibrium even by prolonged heating. However, microstructures of alloys containing from 68 to 69 per cent W after protracted sintering at 1600° C. appear to consist solely of  $\beta$  ( $\text{Fe}_3\text{W}_2$ ) while the liquid formed at the eutectic temperature can be detected in concentrations between 67.5 and 68 per cent W. It seems likely, then, that the composition range of  $\beta$  at 1600° C. does not exceed 1 per cent. The  $\epsilon$  phase, on the basis of chemical analysis, appears to be represented by the formula  $\text{Fe}_2\text{W}$  and has been correspondingly located in the diagram as proposed by Arnfelt.

#### ACKNOWLEDGMENTS

The authors wish to express their appreciation to the Aluminum Company of America for the use of the diffraction apparatus and to Messrs. C. M. Tucker and J. H. Riendeau, who prepared the patterns and assisted in the calculations.

#### DISCUSSION

(*Robert F. Mehl presiding*)

R. F. MEHL, Pittsburgh, Pa.—The care that Mr. Sykes takes in interpreting the so-called typical microscopic structures is very proper. Metallographers frequently assume the presence of a eutectoid or eutectic by what is called a typically eutectic structure. This is dangerous. I have prepared silver-copper alloys falling in composition well within the solid solution fields at high temperatures, which, upon cooling, do not form "typical" Widmanstätten figures, but structures that could be called "typically eutectic." Dr. Gann presented me this week with a photomicrograph of an alloy of magnesium with aluminum in solid solution, which again on cooling precipitated the intermediate Mg-Al phase in such a way as to form a "typically eutectic" pattern. It is necessary therefore to exercise care, and to caution the student to exercise care in the interpretation of photomicrographs, particularly with respect to the identification of typical structures.

O. E. HARDER, Columbus, Ohio (written discussion).—This publication was a welcomed contribution, because I had just been writing a chapter on the Constitution of Iron-tungsten Alloys for the iron-tungsten monograph being prepared in connection with the Alloys of Iron Research.

<sup>12</sup> Reference of footnote 2.

Of these intermediate phases in the iron-tungsten system, it is interesting to note that up to about 1918 at least five intermetallic compounds had been reported in the iron-tungsten system; namely,  $\text{Fe}_4\text{W}$ ,  $\text{Fe}_3\text{W}$ ,  $\text{Fe}_2\text{W}$ ,  $\text{Fe}_3\text{W}_2$  and  $\text{FeW}_2$ . The contribution by one of the present authors in 1926 did much to clarify this system, but there remained considerable uncertainty with reference to the intermediate phases  $\text{Fe}_2\text{W}$  and  $\text{Fe}_3\text{W}_2$ , Arnfelt having reported the existence of both of these phases while Takeda had concluded that  $\text{Fe}_2\text{W}$  did not exist but had suggested the possible existence of another intermediate phase, in the range of about 82 to 90 per cent tungsten, which he designated as "X."

The authors seem to have established conclusively the existence of the intermetallic compound  $\text{Fe}_3\text{W}$ , as well as determined within narrow temperature ranges the temperatures of its formation and also the speed of its formation.

Their experiment, in which an alloy containing 70 per cent of tungsten and 30 per cent of iron sintered 150 hr. at  $1000^\circ\text{C}$ . showed only the low-temperature phase ( $\text{Fe}_2\text{W}$ ), is rather disconcerting, because if alloys of this composition (greater tungsten content than is required for  $\text{Fe}_3\text{W}_2$ ) show only the  $\text{Fe}_2\text{W}$  phase, it would mean that the other intermediate phase,  $\text{Fe}_3\text{W}_2$ , is unstable at a temperature of  $1000^\circ\text{C}$ . However, when it is noted that they observed considerable excess tungsten, one may assume that the system was not in equilibrium and that the more active iron had diffused into the tungsten, forming the iron-rich intermediate phase.

In their test, in which an alloy containing 55 per cent tungsten was heated 5 hr. at  $1075^\circ$  to  $1100^\circ\text{C}$  and found to show excess iron and the low-temperature phase, it should be noted that their results do not seem to agree with their constitutional diagram. As is obvious, the temperature of  $1075^\circ$  to  $1100^\circ\text{C}$ . is above the line drawn for the upper limit of stability of this compound. Their suggestion that the reaction is  $\text{Fe} + \text{W} \rightarrow \text{Fe}_2\text{W} \rightarrow \text{Fe}_3\text{W}_2$  seems questionable.

It is to be regretted that a little more work was not done on the alloy containing 65 per cent of tungsten, which falls between the two intermediate phases, because with properly controlled experiments it should be possible in this alloy to have the two phases present in the same specimen.

Their explanation for the stability of the high-temperature intermediate phase ( $\text{Fe}_3\text{W}_2$ ), once it has been formed, seems satisfactory. Figs. 3 and 4 appear to show that the low-temperature phase  $\text{Fe}_2\text{W}$  has been formed on the surface of the particles of the higher temperature phase. The X-ray examination of these particles after removal of the iron-rich solid solution by an etching attack, in which the etched surface of blocks would be examined, or the residue, might possibly show a surface layer of the low-temperature phase  $\text{Fe}_2\text{W}$ . The authors have done a real service in simplifying and more definitely establishing the iron-tungsten equilibrium diagram.

W. P. SYKES (written discussion).—The interest shown by Dr. Harder has been very gratifying to the authors. His observation regarding the failure of the 70 per cent W specimen (Fe-70W-X-3) to develop the  $\beta$  phase after sintering at  $1000^\circ\text{C}$ . is most pertinent. He has indicated the principal objection to this method of forming alloys; i.e., attaining phase equilibrium by heating or "sintering" below the solidus temperature. The authors feel that Dr. Harder has answered his own question here quite as completely as they might be able to answer it in assuming that the system was not in equilibrium after heating for 150 hr. at  $1000^\circ\text{C}$ . The data certainly offer no proof that the  $\beta$  phase is stable at  $1000^\circ\text{C}$ . We would call attention at this point to the specimen Fe-70W-X-2 which, after sintering at  $1450^\circ\text{C}$ ., showed only the pattern of the  $\beta$  phase. The attempt to convert this  $\beta$  to  $\epsilon$  by reheating at  $1000^\circ\text{C}$ . for 125 hr. was unsuccessful. It appears that the only possibility of proving stability of  $\beta$  at  $1000^\circ\text{C}$ . lies in sintering the metal powders at this temperature for periods much longer than 150 hr. The authors recognize with regret the lack of such data as might have rendered the investigation more complete.

In the second case cited by Dr. Harder, the 55 per cent tungsten alloy, after 5 hr. sintering at 1100° C., showed in the diffraction pattern the lines of  $\epsilon$  together with considerable excess iron. We would call his attention to the fact that 25 hr. sintering at 1100° C. has resulted in the formation of the  $\beta$  phase in this composition (Fe-45-W55-X-4) as required by the constitutional diagram. The suggested reaction  $\text{Fe} + \text{W} \rightleftharpoons \text{Fe}_2\text{W} \rightleftharpoons \text{Fe}_3\text{W}_2$  was based solely upon the sequence of the  $\epsilon$  and  $\beta$  patterns in this alloy after heating at 1100° C. for 5 and 25 hours.

F. N. SPELLER, Pittsburgh, Pa —Has Mr. Sykes any data on the hardness of the precipitation phases he has shown?

W. P. SYKES —No, except that they are hard and brittle. Both are much harder than the solid solution, as indicated by scratch tests.

## Studies upon the Widmanstätten Structure, IV The Iron-carbon Alloys

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(New York Meeting, February, 1933)

THE Widmanstätten figures found in the steels have been long recognized and in some aspects carefully studied,<sup>1</sup> especially as they occur in cast hypoeutectoid alloys. Aside from the practical importance of the structures obtained in the steels by various heat treatments, a study of the characteristics of these figures is interesting because of the rich opportunity the system affords to obtain new data on the mechanism of segregation from solid solutions.

This opportunity is twofold: first, by changing composition within the austenite range the proeutectoid precipitate may be changed from that of ferrite to that of cementite, thus offering the same opportunity for changing the type of precipitate while maintaining the same basic lattice as that afforded by the Cu-Zn alloys;<sup>2</sup> and second, the eutectoid inversion leads upon drastic quenching to the formation of martensite, a Widmanstätten figure of unique interest from the crystallographic viewpoint, particularly in comparison with those formed on slow cooling.<sup>3</sup>

We have, therefore, two types of structure to study: that formed on slow cooling of hypoeutectoid and hypereutectoid alloys, and that formed on quenching hypoeutectoid, eutectoid, and hypereutectoid alloys. For each of these types of structure we require the crystallographic plane in the mother austenite along which the precipitate forms (we shall see that the precipitates in these alloys are invariably platelike in form), and also the orientation of the precipitate upon this plane. Some of these

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<sup>1</sup> R. F. Mehl and C. S. Barrett: Studies upon the Widmanstätten Structure, I.—Introduction. The Aluminum-silver and the Copper-silicon Systems. *Trans. A.I.M.E.* (1931) **93**, Inst. Metals Div., 78–122. References 3 to 7.

<sup>2</sup> R. F. Mehl and O. T. Marzke: Studies upon the Widmanstätten Structure, II. The  $\beta$  Copper-zinc and the  $\beta$  Copper-aluminum alloys *Trans. A.I.M.E.* (1931) **93**, Inst. Metals Div., 123–161.

<sup>3</sup> In view of the work of Kurdjumow and Sachs [Über den Mechanismus der Stahhartung. *Ztsch. f. Phys.* (1930) **64**, 325–343], we must classify the martensitic structure as a Widmanstätten figure. See discussion on this point, reference 1 above, reference 8 and discussion therein.

data are already available from the work of Belaiew and of Kurdjumow and Sachs, as will be shown; it is the intention of this contribution to complete the data as far as possible.

### THE $\gamma \rightarrow \alpha$ TRANSFORMATION IN PURE IRON

The crystallographic mechanism for the transformation of  $\gamma$  into  $\alpha$  iron has not yet been completely demonstrated. The details of this mechanism seem certain by analogy with the orientation relationships between  $\gamma$  and  $\alpha$  iron found in martensite by Kurdjumow and Sachs (*loc. cit.*), by analogy with those between austenite and ferrite in slowly cooled hypoeutectoid steels here demonstrated, and from the partial solution available for pure iron. The mechanism for the transformation of  $\gamma$  into  $\alpha$  we shall call the "basic mechanism," and discuss it at this point in order to facilitate the presentation of the work as a whole.

We find, consistently enough, that pure iron under suitable quenching treatment will exhibit a Widmanstätten figure<sup>4</sup> in which the octahedral planes of the original gamma iron are delineated in the pattern (judging only from the number of directions exhibited and by analogy with the figures obtained in slowly cooled hypoeutectoid steels) This Widmanstätten figure is visible on the unetched surface and also may be produced by suitable etching after removing the original surface by polishing. The pattern visible upon the unetched surface is a relief pattern which doubtless originates in the shearing action that accompanies the transformation (see below), whereas that found after polishing and etching is developed very probably by a differential etching action caused by the internal strains residual from the transformation and by a multiplicity of ferrite orientations.

It was suggested in the first paper in this series (ref. 1) that the crystallographic mechanism by which Widmanstätten figures form may be considered as a transformation of one plane of atoms in the parent lattice into one plane of atoms in the new lattice to which it is closely similar and into which it may transform with very little alteration in atom positions, followed by or simultaneous with a shearing of neighboring parallel atom planes into proper positions for the new lattice. Independently Kurdjumow and Sachs (ref. 3), whose results had been largely predicted by Jeffries as stated below, proposed this type of mechanism to explain the orientations of ferrite and of the tetragonal intermediate state found in martensite.

The arrangement of atoms upon the (111) $\gamma$  plane is shown in Fig. 1a by circles, that upon the (011) $\alpha$  plane by small dots. The similarity in

<sup>4</sup> A. Sauveur and A. Chou: The Gamma-alpha Transformation in Pure Iron. *Trans. A.I.M.E.* (1929) **84**, Iron and Steel, 350. Professor Sauveur had predicted the result of this experiment in The Widmanstätten Structure of Iron Alloys. *Proc. Amer. Phil. Soc.* (1927) **66**, 267.

spacing here is evident. It was suggested by McKeehan<sup>5</sup> and demonstrated by Kurdjumow and Sachs (for martensite) that these two planes—generally designated as “conjugate planes” in the present series of papers—may be superimposed in six different ways, by bringing into coincidence in turn each of the three  $[110]\gamma$  directions that lie in the  $(111)\gamma$  plane with one of the two  $[111]\alpha$  directions that lie in the  $(011)\alpha$  plane. The

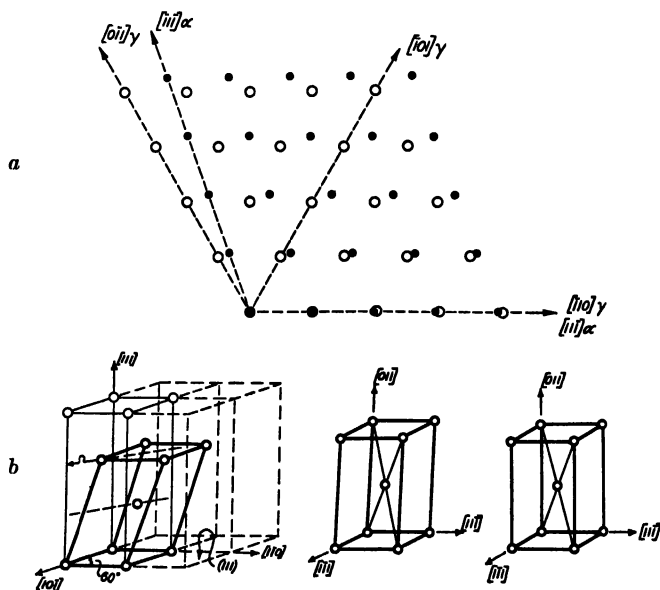


FIG 1—LATTICE TRANSFORMATIONS IN MARTENSITIC STEELS

a Atomic arrangements on austenite  $(111)$  and ferrite  $(011)$  planes. Circles represent iron atoms of austenite; dots represent iron atoms of ferrite.

b. Left: Atomic arrangement on adjacent austenite  $(111)$  planes. Center: Prism shown at left after transformation to the body-centered tetragonal intermediate phase. Right: Prism shown at left after complete transformation to  $\alpha$ .

atoms on these two types of direction are very similar in spacing. Accordingly, upon each plane of the type  $\{111\}\gamma$  we may have six distinct orientations of the plane  $\{110\}\alpha$ . Since there are 4 planes of the type  $\{111\}\gamma$ , a total of 24 orientations of  $\alpha$  will result. The specifications for this transformation may then be written as of the type

$$\begin{aligned}(111)\gamma &\parallel (011)\alpha \\ [110]\gamma &\parallel [11\bar{1}]\alpha\end{aligned}$$

The alteration in atom pattern accompanying the transformation, as shown in Fig. 1a, may be considered as a shear—a movement of the  $\gamma$  atoms in the  $[\bar{1}10]\gamma$  direction, accompanied by a slight displacement normal to this direction.

<sup>5</sup> Discussion to article referred to in footnote 1.



The behavior of atoms on neighboring (111) $\gamma$  planes is represented in Fig. 1b, which has been adapted from a later work by Sachs.<sup>6</sup> The basal plane here is the (111). Atoms on four (111) planes are indicated, and we may express the arrangement of atoms on three layers by a sequence A B C A B C . . . , to indicate that in every fourth plane the atoms simply lie above those of the first. During the transformation these planes move parallel to themselves, as shown by the arrow in Fig. 1b, a shearing action, coming eventually into the sequence A B A B . . . , which is the proper sequence for atoms upon {110} planes in a body-centered cubic lattice. Accompanying this shear is a slight decrease in interplanar distance.

The unit prism in the first diagram in Fig. 1b becomes, during the transformation in martensitic steels, the prism shown next to the right. This prism is one drawn within the body-centered tetragonal lattice observed as an intermediate stage in the  $\gamma \rightarrow \alpha$  transformation in martensitic steels: Ultimately the prism becomes that shown in the right of Fig. 1b, now representing a prism drawn within the body-centered cubic lattice characteristic of  $\alpha$ Fe. The absolute values for the movement of atoms described in this section may be readily calculated from the known lattice parameters.

## IRON-CARBON ALLOYS

### *Structures Formed on Slow Cooling of Hypoeutectoid Alloys*

*Formation and Outward Form of Precipitate.*—When austenite with less than 0.9 per cent C cools through the transformation range, it rejects ferrite (Fig. 2). This ferrite may, depending upon the rate of cooling, form preferentially at the grain boundary, giving rise to a "network" structure, or it may form at the grain boundary and within the grain also, giving rise to the Widmanstätten structure.

It is now generally agreed that a large grain size in the original austenite is favorable to the development of the Widmanstätten figure, apparently because there is less opportunity in the larger grains for the operation of diffusion to and from the grain boundaries.<sup>7</sup>

After the formation of the first precipitate, whether at the grain boundary or within the grain, the subsequent rate of cooling is of great importance in determining the final microstructure. Although there is some uncertainty, it seems that a very slow rate of cooling will tend to mass the intergranular and intragranular ferrite, forming islands of ferrite,

<sup>6</sup> G. Sachs: Allgemeine Gesetzmässigkeiten der Gefüge- und Eigenschaftsänderungen bei Umwandlungsvorgängen. *Ztsch. f. Metallkunde* (1932) **24**, 241.

<sup>7</sup> H. M. Howe: Life History of Network and Ferrite Grains in Carbon Steel. *Proc. Amer. Soc. Test. Mat.* (1911) **11**, 263-386.

N. T. Belaiew: On the Genesis of the Widmanstätten Structure in Meteorites and in Iron-Nickel and Iron-Carbon Alloys. *Mineral Mag.* (1923-1925) **20**, 173.

and that a faster rate of cooling will tend to preserve that form generated during the decomposition or precipitation. The effect of the rate of cooling is apparently bipartite: to control the manner in which the precipitate is rejected—whether to the boundary or within the grain—and to control the degree of massing or coagulation after the precipitate has

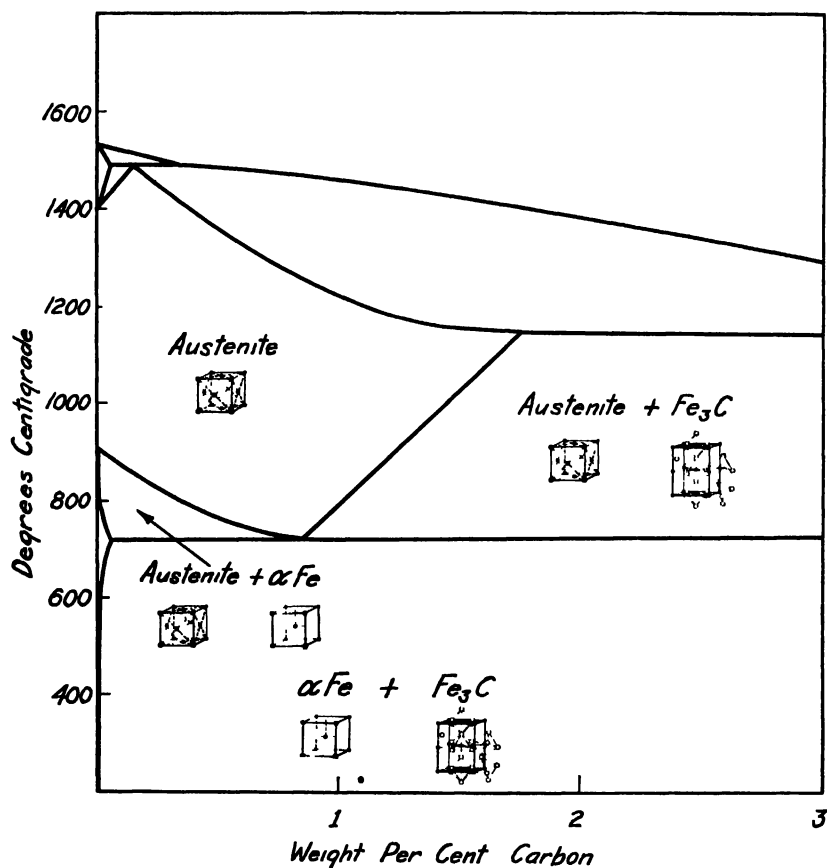


FIG 2.—THE IRON-CARBON SYSTEM.

formed. Since the precipitation process extends progressively over a wide temperature interval, both processes must operate simultaneously within this temperature interval, and it becomes difficult to separate the two effects clearly.<sup>8</sup>

<sup>8</sup> This subject was discussed briefly in the first paper of this series (R. F. Mehl and C. S. Barrett: Reference of footnote 1). The various factors entering into the problem were reviewed some years ago by Belaiew (N. T. Belaiew: Reference of footnote 7) from whose account the discussion in the above paper was taken. Professor Sauveur, in commenting on this paper, pointed out that the work of A. Sauveur and C. H. Chou [Influence of Rate of Cooling on Dendritic Structure and Microstructure

The effect of the rate of cooling upon the degree of perfection of the final Widmanstätten figure has been experimentally studied by Howe,<sup>9</sup> by Krivobok,<sup>10</sup> by Sauveur and Chou,<sup>11</sup> by Kase,<sup>12</sup> and especially by Carpenter and Robertson<sup>13</sup> who also studied the effect of variations in carbon content. Howe, Kase, and Belaiew held that "a very slow rate of cooling" tends to round the original Widmanstätten plates of ferrite into islands, whereas Sauveur and Chou held that "a slow rate of cooling" (an ingot of possibly 150 grams, furnace cooled) gives the best defined figure, and Krivobok found the best defined figures in very slowly cooled alloys. Carpenter and Robertson, by interrupting the precipitation by quenching, were able to observe the first stages of the precipitation, and found that in low-carbon steels (0.10 per cent C), rapidly cooled, the early stage may be a well defined figure which with further growth becomes thickened and indefinite in outline whereas slow rates gave only intergranular ferrite; with increasing carbon it was found easy by fast cooling to obtain a well formed figure, whereas slow cooling led to indistinct structures. Apparently further study is needed, particularly with respect to the effect of definite (not relative) rates of cooling and with respect to the effect of austenite grain size and of impurities or alloying elements.<sup>14</sup>

It is possibly unnecessary now to state that the ferrite in this Widmanstätten figure is in the form of true plates. This fact is vouchsafed by numberless photomicrographic studies of cast steel.<sup>15</sup>

It might be well to point out that the network ferrite frequently extends towards the center of the austenite cell in "needles" or "spines."

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of Some Hypoeutectoid Steel. *Trans. A.I.M.E.* (1930) **90**, Iron and Steel, 100.] did not bear out Belaiew's contentions. Nor does the work of Professor Krivobok [Secondary Crystallization in Iron-Carbon Alloys. *Trans. Amer. Soc. Steel Treat.* (1924), 457] bear out Belaiew's conclusions.

<sup>9</sup> H. M. Howe: Reference of footnote 7.

<sup>10</sup> V. N. Krivobok: Reference of footnote 8.

<sup>11</sup> A. Sauveur and C. H. Chou: Reference of footnote 4.

<sup>12</sup> T. Kase: On the Widmanstätten Structure in Iron-Carbon and Iron-Nickel Alloys. *Sci. Repts. Tohoku Imp. Univ.* (1925) **14**, 537.

<sup>13</sup> H. C. H. Carpenter and J. M. Robertson: The Formation of Ferrite from Austenite. Iron and Steel Inst. *Advance Copy* (May, 1931).

<sup>14</sup> The formation of Widmanstätten ferrite has also been studied by J. P. Arend [Metallographische Forschungen in Giessereiwesen. *Stahl und Eisen* (1917) **37**, 393] and by P. Oberhoffer and F. Weisgerber [Die Bedeutung des Glühens von Stahlformguss. *Stahl und Eisen* (1920) **40**, 1433]. Arend and Oberhoffer and Weisgerber also studied the physical properties of hypoeutectoid alloys exhibiting a Widmanstätten structure. These various articles are briefer than those previously quoted and need not be mentioned further.

<sup>15</sup> H. Hanemann and A. Schrader [Atlas Metallographicus. Lieferung 5 (1927)] have published remarkably good photographs of Widmanstätten structures in cast steel.

Such ferrite doubtless bears the same relationship in orientation to the original austenite as the pronouncedly Widmanstätten ferrite. Grain-boundary ferrite is very similar in appearance to the grain-boundary segregates in the brasses (ref. 2); it seems highly probable that, as in the brasses, the orientation of the grain-boundary segregate in these alloys is not random but determined by the orientation of the parent austenite.

*Crystallography of Participating Phases.*—The  $\alpha$  phase, ferrite, is body-centered cubic in structure. The side of the unit cube,  $a_0$ , for pure iron is reported by Mayer<sup>16</sup> to be  $2.8610\text{\AA}$  at room temperature. Data on the effect of carbon in solid solution upon this value are not available, but the effect is probably small, judging from the effect in  $\gamma$  iron. Since highly precise values for lattice parameters are in general unnecessary in this work, we may take a value of  $a_0 = 2.86\text{\AA}$  as satisfactory.

The  $\gamma$  phase, austenite, is face-centered cubic in structure. The side of the unit cube,  $a_0$ , for pure  $\gamma$  iron, has been approximated by Öhman<sup>17</sup> by extrapolation from values for Fe-Mn alloys as  $a_0 = 3.562\text{\AA}$  at room temperature. The variation in  $a_0$  with increasing carbon has been studied by Westgren and Phragmén,<sup>18</sup> by Fink and Campbell,<sup>19</sup> and by Honda and Sekito.<sup>20</sup> These studies indicate that  $a_0$  increases approximately linearly with weight per cent carbon up to  $3.629\text{\AA}$  at 1.7 per cent C. Furthermore, density determinations indicate that the carbon is interstitial in the  $\gamma$  lattice and distributed at random within this lattice.

*Determination of Plane of Precipitation.*—This we owe to Belaiew,<sup>21</sup> who prepared and studied an extremely well formed figure in a steel with 0.55 per cent C. Belaiew counted the number of directions shown by the ferrite traces in 20 grains, finding a maximum of 4, which in itself is proof of the octahedral orientation of the ferrite plates—if it is assumed that these plates are actually parallel to certain crystallographic planes in the original austenite. Belaiew also measured the angles between these traces and showed them to be consistent with permissible angles calculated on the basis of an octahedral precipitation.<sup>22</sup>

<sup>16</sup> G. Mayer: Die Gitterkonstante von reinem  $\alpha$ -Eisen. *Ztsch. Kristallographie* (1929) **70**, 383–4.

<sup>17</sup> E. Öhman: Röntgenographische Untersuchungen über das System Eisen-Mangan. *Ztsch. f. phys. Chem.* (1930) **8**, 81–110.

<sup>18</sup> A. Westgren and G. Phragmén: X-ray Studies on the Crystal Structure of Steel, II. *Jnl. Iron and Steel Inst.* (1924) **109**, 159

<sup>19</sup> W. L. Fink and E. D. Campbell: Influence of Heat-treatment and Carbon Content on the Structure of Pure Iron-Carbon Alloys. *Trans. Amer. Soc. Steel Treat.* (1926) **9**, 717–49.

<sup>20</sup> K. Honda and S. Sekito: The X-ray Investigation of the Formation of Martensite. *Sci. Repts. Tohoku Imp. Univ.* (1928) **17**, 743–760.

<sup>21</sup> N. T. Belaiew: Inner Structure of the Crystal Grain as Revealed by Meteorites and Widmanstätten Figures. *Jnl. Inst. Metals* (1923) **29**, 379.

<sup>22</sup> Belaiew presented a table of angles formed by the intersection of a plane with an octahedron in five-degree intervals of the two defining angles. *Stereographic*

It is certain, therefore, that ferrite forms in plates upon the  $\{111\}$  planes of austenite.

*Determination of Orientation of Ferrite Plates.*—The experimental determination of the orientation of the ferrite in a coarse Widmanstätten figure promised at first to be an easy problem: the ferrite plates are relatively large and there are many methods for the determination of the orientation of crystallites that should be applicable. This was not borne out by experimentation, however. It might be expected that the X-ray methods used by Kurdjumow and Sachs (see page 243) would be even more easily applicable to this case than to martensite, but lengthy experimentation failed to give photograms that could be analyzed. The use of Neumann bands and of cleavage planes (upon fracture at very low temperatures) likewise failed, by reason of insufficient development. Since, as we have indicated above, the ferrite should have a total of 24 separate orientations, the use of etch pits for specular reflection on a reflection goniometer is not feasible because of the multiplicity of reflection. It finally proved possible to obtain the desired result by the study of the traces of etch pits.

The production of sharply defined etch pits in the ferrite lamellae proved far more difficult than in single crystals of "pure" iron. After much effort it was found that by proper use copper-ammonium chloride would develop properly defined pits. Although it is generally assumed that etch pits in iron define the cube  $\{100\}$  faces, it was found that this reagent develops dodecahedral  $\{110\}$  faces.<sup>23</sup>

Since all of the four  $\{111\}$  planes in austenite are equivalent, the problem may be simplified by studying the orientation of the ferrite upon only one of these planes. Accordingly a sample of cast steel with 0.4 per cent C.<sup>24</sup> showing a well defined Widmanstätten figure in very large austenite cells was cut as nearly parallel to a  $\{111\}$  plane as possible; this gave large islands in the Widmanstätten ferrite lying parallel to the plane of cut (Fig. 3). The orientation of the original austenite was then established by determining the angles formed by all four sets of ferrite lamellae on two surfaces of polish at right angles, and expressed upon a stereographic projection (Fig. 4).

By analogy with meteorites and with the atomic transformation mechanism postulated in part by Jeffries and by McKeehan, and demonstrated for the martensite transformation by Kurdjumow and Sachs, we may expect the ferrite to be so oriented that a  $\{110\}$  plane will lie parallel to a  $\{111\}$  plane in the austenite and in these planes the  $[111]$  directions in

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methods are used throughout the present work because of their greater flexibility and elegance.

<sup>23</sup> D. W. Smith and R. F. Mehl: *Metals & Alloys* (March, 1933).

<sup>24</sup> Of the following analysis: 0.41 per cent C, 0.68 Mn, 0.029 P, 0.038 S, 0.19 Si.

the ferrite will lie parallel to the  $[110]$  directions in the austenite, giving a total of six ferrite orientations on each  $\{111\}$  plane in the austenite.



FIG. 3.—WIDMANSTATTEN FIGURE STUDIED IN HYPOEUTECTOID ALLOY  $\times 35$ .

Accordingly we may expect to find six separate orientations among the ferrite islands in Fig. 3.

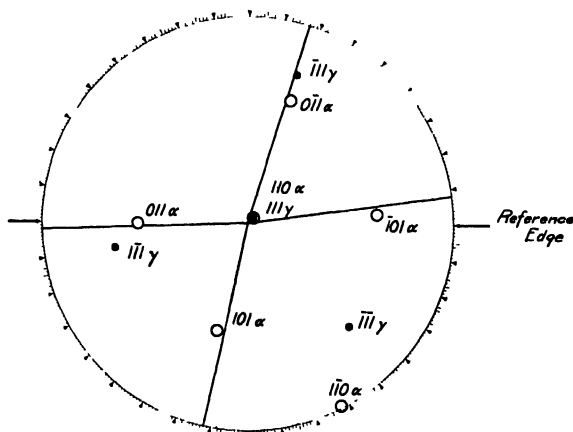


FIG. 4.—STEREOGRAPHIC REPRESENTATION OF ORIENTATION OF ORIGINAL AUSTENITE CELL AND ONE OF SIX POSSIBLE ORIENTATIONS OF FERRITE UPON AUSTENITE  $\{111\}$  PLANE, TOGETHER WITH ONE SET OF ETCH-PIT TRACE NORMALS.

Dots are poles of austenite  $\{111\}$  planes; circles are poles of ferrite  $\{110\}$  planes; radii are normals to traces of etch pits.

Since the reagent chosen for etch pit formation develops the dodecahedral planes, we may expect to create five of the six dodecahedral planes

TABLE 1.—*Angles of Etch-pit Traces*

Case	Predicted	Observed	Deviation	Obs	Dev.	Obs	Dev.	Obs	Dev.	Obs.	Dev.
(110) $\alpha$    (111) $\gamma$	29	33	+ 4	31	+ 2						
$[\bar{1}11]\alpha$    $[\bar{1}01]\gamma$	36	34	- 2	38	+ 2						
	101	101	0	106	+ 5						
	104	117	+13	114	+10						
	157										
Average total deviation			$4\frac{3}{4}$		$4\frac{3}{4}$						
Average net deviation			$+3\frac{3}{4}$		$+4\frac{3}{4}$						
(110) $\alpha$    (111) $\gamma$	40	43	+ 3	39	- 1	38	- 2	38	-2	37	-3
	46	48	+ 2	45	- 1	47	+ 1	44	-2	41	-5
$[\bar{1}\bar{1}1]\alpha$    $[\bar{1}\bar{1}0]\gamma$	112	116	+ 4	108	- 4	110	- 2	109	-3	112	0
	114	123	+ 9	119	+ 5	126	+12	116	+2	123	+9
	168										
Average total deviation			$4\frac{1}{2}$		$2\frac{3}{4}$		$4\frac{1}{4}$		$2\frac{1}{2}$		$4\frac{1}{4}$
Average net deviation			$+4\frac{1}{2}$		$- \frac{1}{4}$		$+2\frac{1}{4}$		$-1\frac{1}{4}$		$+ \frac{1}{4}$
(110) $\alpha$    (111) $\gamma$	40	47	+ 7								
$[\bar{1}\bar{1}1]\alpha$    $(\bar{1}10)\gamma$	46	50	+ 4								
	98										
	152	146	- 6								
	153	156	+ 3								
Average total deviation .			5								
Average net deviation			+ 2								
(110) $\alpha$    (111) $\gamma$	50	55	+ 5	48	- 2	48	- 2	52	+2	47	-3
$[\bar{1}\bar{1}1]\alpha$    $[0\bar{1}1]\gamma$	55	62	+ 7	56	+ 1	58	+ 3	55	0	61	+6
	107										
	161	155	- 6	156	- 5	151	-10	152	-9	152	-9
	164	159	- 5	166	+ 2	157	- 7	158	-6	159	-5
Average total deviation			$5\frac{3}{4}$		$2\frac{1}{2}$		$5\frac{1}{2}$		$4\frac{1}{4}$		$5\frac{1}{4}$
Average net deviation			$+ \frac{1}{4}$		- 1		- 4		$-3\frac{1}{4}$		$-2\frac{3}{4}$
(110) $\alpha$    (111) $\gamma$	38										
$[\bar{1}\bar{1}1]\alpha$    $[0\bar{1}1]\gamma$	90	88	- 2	90	0						
	93	98	+ 5	96	+ 3						
	161	163	+ 2	170	+ 9						
	164	168	+ 4	174	+10						
Average total deviation			$3\frac{1}{4}$		$5\frac{1}{2}$						
Average net deviation			$+2\frac{1}{4}$		$+5\frac{1}{2}$						
(110) $\alpha$    (111) $\gamma$	50										
$[\bar{1}\bar{1}1]\alpha$    $[\bar{1}01]\gamma$	101	85	-16	92	- 9						
	104	101	- 3	105	+ 1						
	173	170	- 3	175	+ 2						
	178	175	- 3	177	- 1						
Average total deviation . .			$6\frac{1}{4}$		$3\frac{1}{4}$						
Average net deviation .			$-6\frac{1}{4}$		$-1\frac{1}{4}$						

in each of the ferrite islands, leaving five traces upon the surface of polish, for the sixth plane should lie parallel to the surface of polish.

These expectations were realized in the experimental work. Satisfactory etch pits were developed and measured in 17 different ferrite islands. The data are assembled in Table 1, and one set, the fourteenth in Table 1, represented stereographically in Fig. 4.

Only four etch-pit traces are represented in Table 1 for each case; the fifth trace, corresponding to the fifth dodecahedral plane, was always found but not in a well developed state. By prediction this direction was generated in each case by a dodecahedral plane nearly perpendicular to the surface of polish; apparently this condition is not suitable for the development of a well defined plane and resultant trace. The type of pit produced and measured is shown in Fig. 5; the technique of producing sharply defined pits has been described elsewhere (ref. 21). The average position of each etch-pit trace was approximated from a number of well formed pits by means of a straight edge.

Table 1 may perhaps most easily be understood by reference to Fig. 4. In this diagram the orientation of the original austenite is shown by heavy dots representing the  $\{111\}\gamma$  poles. The particular pole (111) does not come exactly at the center of the circle, for the piece was not cut quite parallel to this plane. The dodecahedral plane in the ferrite is made parallel to the octahedral plane in the austenite by the superimposition of the projections  $(110)\alpha$  and  $(111)\gamma$ . The positions of the remaining  $\{110\}\alpha$  poles are fixed in position with respect to the orientation of the austenite lattice by a superimposition (not shown in the figure) of the directions  $[\bar{1}11]\alpha$  and  $[0\bar{1}1]\gamma$ . The diagram thus represents one of the six predicted orientations. The radii in this figure represent normals to the traces of the etch pits, and should—if the proper individual of the six orientations has been chosen—include the  $\{110\}$  poles. This is true, within an experimental error of several degrees, for the four traces measured; the normal to the poorly developed fifth was found to fall near the  $(1\bar{1}0)$  poles, but was unsuitable for measurement, for the reasons stated.

The 17 individual cases measured have been allocated among the six groups in Table 1. These groups naturally divide themselves into three pairs, the first and second, third and fourth, and fifth and sixth. Allocation to proper pairs could be made with great confidence, but with less confidence to a single member of a pair. The justification for the allocation made may be seen in the deviations from the predicted angles calculated for each case. It appears to the authors that the assumed crystallographic relationship between the  $\gamma$  and  $\alpha$  lattices is confirmed by these data.

### *Hypereutectoid Alloys*

*Formation and Outward Form of Precipitate.*—Here also it is agreed that a large grain size in the original austenite is favorable to the development of the Widmanstätten figure, and also that an extremely slow rate of





FIG. 5.—ETCH PITS IN FERRITE IN HYPOEUTECTOID ALLOY.

FIG. 6.—CEMENTITE PLATES, ETCHED WITH BOILING SODIUM PICRATE, THEN BRIEFLY WITH 10 PER CENT NITAL.  $\times 1500$ .



FIG. 7—CEMENTITE PLATES ETCHED AS FIG. 6.  $\times 1500$   
FIG. 8—CEMENTITE PLATES ETCHED AS FIG. 6.  $\times 1500$ .

cooling can tend to mass the cementite into islands.<sup>25</sup> Howe and Levy showed that the crystallization of  $\text{Fe}_3\text{C}$  into intragranular plates (which they as others assumed to be Widmanstätten in nature) is slower, more sluggish, than that of ferrite in hypoeutectoid alloys; accordingly an even slower rate of cooling is necessary to give this figure a distinct form.<sup>26</sup>

It has been rather generally assumed that cementite, like ferrite, precipitates parallel to the octahedral planes of austenite.<sup>27</sup> This will be shown to be incorrect.

Widmanstätten cementite is ordinarily correctly understood as plate-like in outward form, though the term acicular is frequently used to describe it. The work described below may serve to remove any remaining doubts on that score. At low magnifications (Fig. 11) these plates appear quite flat, and their traces on the surface of polish quite straight. At high magnifications, however, the structure of the plates surprisingly appears complicated.

Proper etching reveals the fact that seemingly single plates are really laminated in a plane often apparently parallel to the surface of the plate. These laminations, however, are not perfectly plane, but tend to follow a somewhat tortuous course, though the gross plate may take a rather well defined direction (Fig. 6). The laminations often are not closely in registry but separated appreciably (Fig. 7). Frequently a plate apparently flat at low magnifications is found to be curved or to have a corrugated fine-structure at high, sometimes, though not always, coincidental with the impingement of the other plates (Fig. 7). This serrated structure is apparently a corrugation along one direction, judging from the surface structure of a plate separated from the pearlite matrix by electrolytic dissolution (Fig. 9). Occasionally plates are found built up of laminations in a step-wise fashion (Fig. 8), in which the average direction of the plate traces deviates greatly from the directions of the individual laminations.

The reasons for the distortion observed in the plates are not yet wholly evident. The volume change at the eutectoid inversion in all probability is the chief factor, but the disturbance in the cementite plates is in the nature of a corrugation along one direction only, judging from Fig. 9 and from the X-ray diffracting properties of the plate reported in a later

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<sup>25</sup> H. M. Howe and A. G. Levy: The Life History of Pro-eutectoid Cementite. *Proc. Internat. Assn. Test. Mat.* (1910-12) **2**, II.

<sup>26</sup> The formation of intragranular plates of cementite has been studied by J. O. Arnold and L. Aitchison [Notes on the Solubility of Cementite in Hardenite. *Engineering* (1912) **93**, 713], by N. G. Ilyine [Etude sur les formes sous lesquelles la cementite se presente dans l'acier a outils hypereutectique suivant son traitement thermique. *Rev. Mét.* (1917) **14**, 83].

<sup>27</sup> H. M. Howe: *The Metallography of Steel and Cast Iron*, 202, 279. New York, 1916. McGraw-Hill Book Co.

section, whereas a more general type of distortion would be expected as a result of such a process. It might be noted here that the ferrite plates studied in hypoeutectoid steels (Fig. 3) likewise show some scatter from



FIG 9—SURFACE OF CEMENTITE PLATE REMOVED FROM MATRIX.  $\times 150$   
SHOWING STRIATIONS HORIZONTAL IN THE CUT.

the ideal  $\{111\}$  orientation, possibly also because of distortion during the eutectoid inversion.

*Crystallography of Participating Phases.*—The crystallography of the  $\gamma$  phase has been discussed above. Cementite,  $\text{Fe}_3\text{C}$ , has been known to be orthorhombic for some time. Westgren and Phragmén<sup>28</sup> prepared X-ray photographs but did not determine atom positions. Hendricks<sup>29</sup> recently analyzed Westgren's photographs and derived a complete structure. Westgren and Phragmén had shown the structure to be orthorhombic, with four molecules of  $\text{Fe}_3\text{C}$  in the unit cell, and had determined the dimensions of this cell. Hendricks derived the atom positions and identified the structure as one of the coordination type. His structure is given in Fig. 10, drawn to show the octahedra of iron atoms (open circles) surrounding the central carbon atoms (full circles).

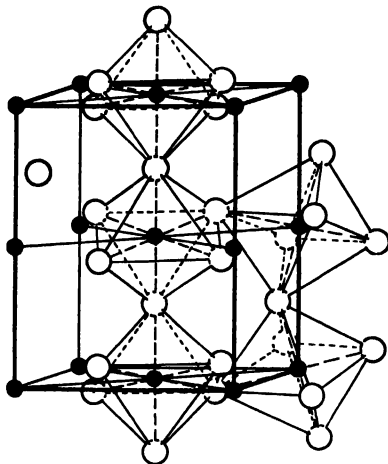


FIG. 10.—CEMENTITE LATTICE. (After S B Hendricks)

The dimensions of the cell represented in Fig. 10 were determined as  $a = 4.518$ ,  $b = 5.069$ ,  $c = 6.736$ .

<sup>28</sup> A. Westgren and G. Phragmén: X-ray Studies on the Crystal Structure of Steel. *Jnl. Iron and Steel Inst.* (1922) **105**, 24; X-ray Studies on the Crystal Structure of Steel, II. *Idem.* (1924) **109**, 159.

<sup>29</sup> S. B. Hendricks: The Crystal Structure of Cementite. *Zisch. f. Kristallographie* (1930) **74**, 534.

A different structure has been proposed by Shimura<sup>30</sup> but Hendrick's solution is probably the correct one<sup>31</sup> and will be used here.

*Determination of Plane of Precipitation. Experimental.*—A series of ingots was prepared, roughly  $2\frac{1}{4}$  by  $2\frac{1}{4}$  by 10 in., from steel melted in an induction furnace. These ingots were cast in dry sand without addition of deoxidizer, in order to produce as large an austenitic grain size as possible; the ingots, accordingly, were very porous. Each ingot was cut into slabs and inspected for large cells containing numerous well defined cementite plates. The ingot finally selected contained 1.3 per cent C. From this ingot was cut a small piece containing a cell approximately 4 mm. in diameter. This piece was trimmed and polished on three sides nearly at right angles, with the cell concerned in the corner. Hereafter these three faces of this cell will be referred to as "surface 1," "surface 2," and "surface 3." Surface 4 was cut roughly parallel to surface 2.

The determination of the plane of precipitation can be performed most easily and directly when the orientation of the parent solid solution can be directly determined and the angular position of the precipitate plates in space compared with corresponding positions of the atomic planes of the parent solid solutions. Such a technique is not possible with the hyper-eutectoid steels (nor with the hypoeutectoid), unless the orientation of the original austenite grain is determined at temperatures where austenite is stable—a very difficult feat, for the original austenite matrix on cooling transforms to pearlite at an awkwardly high temperature. In such instances indirect methods must be adopted.

If, however, the angular positions of the cementite plates in space can be determined, and if a sufficient number of plates can be studied for this purpose, the angles which these plates form among themselves, and the symmetry relationships exhibited by these angles, may be used to derive the orientations of the original austenite. In order to obtain these interplate angles, it is necessary to trace individual plates around an edge (as from surface 1 to surface 2) and from the angles which the traces of a plate on the two surfaces make with the edge to calculate the normal to each plate, which defines its position in space.

This was the technique adopted. Surfaces 1, 2 and 3 were given a fine polish, with special attention to maintaining very sharp edges between the surfaces. Each side was then photographed and the finished photographs matched along the edge to discover the "needles" continuous across the edge. After this first match was obtained, each edge was studied visually in a microscope with both surfaces illuminated at an angle of  $45^\circ$  to the optical axis of the microscope, in order to confirm by

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<sup>30</sup> K. Honda: Space Lattice of Cementite. *Metal Progress* (1930) 18, 87.

<sup>31</sup> A. Westgren: Iron, Carbon, and Nitrogen. *Metal Progress* (July, 1931) 52.

direct visual examination the continuity of the suspected traces across the edge.

It was found impossible to prepare two sharp edges (between surfaces 1 and 2, and 1 and 3) at the same time, and for this reason only two

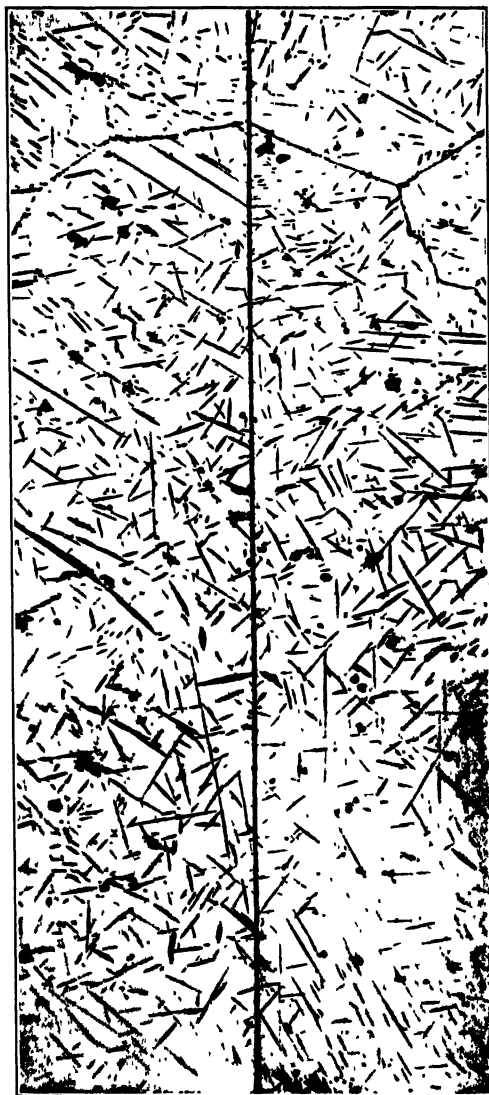


FIG. 11.—COMPOSITE PHOTOMICROGRAPH SHOWING CEMENTITE PLATES IN TWO SURFACES OF POLISH AT RIGHT ANGLES  $\times 165$

surfaces were studied at one time. Thus plates were first traced from surface 1 to surface 2, and the specimen then repolished to get a sharp edge between surfaces 1 and 3, etched, and other plates traced around this edge. Two edges studied in this way gave only about 12 separate plates.

In order to procure a larger number of plate positions, the operation just described was repeated, with a layer of the specimen removed each time to get a new group of plates at a lower level. Four such operations were performed between surfaces 1 and 2 and four between surfaces 1 and 3, resulting in a crop of 103 plates definitely traced across an edge and therefore fixed in space. Fig. 11 shows two surfaces studied in this way.

In determining the angular positions of the traces on the several surfaces, the specimen was held rigidly on the microscope stage with surface 4 flush against a stop. The photographic plates were fixed in the plateholder so that their lower edges always coincided closely with the lower edge of the frame of the plateholder. Photographs taken of surface 1 in this way maintained a constant position with respect to the piece observed. The positions of the traces were then measured with the edge of the photographic plate as a reference line.

On the developed photographic plate the angles formed by the traces were measured with the edge of the piece (between surface 1 and 2, or 1 and 3) as a reference line. The angle formed by this edge with the lower edge of the photographic plate was then measured and each angular position of trace corrected in order to refer all angles to a constant basal line, since the eight operations of polish somewhat changed the angle between the edge of the piece and the lower edge of the photographic plate. Thus each trace angle measured against an edge was corrected to refer to a common basal line. The angle that the three surfaces formed with one another was maintained nearly equal to  $90^\circ$ , but it may be shown that a slight deviation from  $90^\circ$  introduces no appreciable variation in the final positions of the plotted stereographic points; an inspection of the angle, to ascertain that it did not vary over one degree from  $90^\circ$ , sufficed to maintain accuracy in the stereographic plot.

The measurements of the angles of the cementite traces against the piece edges are listed in Table 2 for each of the eight operations. The angles listed in Table 2 were measured upon the photographic print in a counter-clockwise direction from the edge, and involve the usual photographic reversal of image and therefore of the true angle on the plate. Table 2 also lists the angle formed by the reference edge against the lower edge of the photographic plate, measured counter-clockwise on the photographic plate from the basal line—the lower edge of the photographic plate.

These measurements, corrected for photographic reversal, were plotted stereographically with surface 1 in the plane of the projection, after each set of angles (angles from each operation) was corrected for the angle formed between the edge and the basal line, and after correction had been made for the photographic reversal. The normals to the angles of the traces on surface 1 appeared on the stereographic projection as straight lines through the center point, and the planes containing the normals of the traces on the other side (2 or 3) as great circles. The intersections

TABLE 2.—*Result of Stereographic Plot of 103 Cementite Plates*  
*First Operation* (Angle of edge with basal line = 2°)

	1	2	3	4	5	6
Surface 1: 60°-30'	151°-31'	34°-30'	88°	123°-30'	110°	
Surface 2:	96	116	60-30	44-30	142	103-30

*Second Operation* (Angle of edge with basal line = 91°)

	1	2	3	4	5	6	7	8	9
Surface 1:	64	150	91-30	108	150	109	22	119	151-30
Surface 3:	60-30	100	157	100-30	74-30	73-30	59	67	85

*Third Operation* (Angle of edge with basal line = 2°-30')

	1	2	3	4	5	6	7	8	9	10
Surface 1:	64-30	102	57-30	130	52-30	51	114	102	101-30	57-30
Surface 2:	24	106	91	148	83	82-30	95	133-30	107	104

*Fourth Operation* (Angle of edge with basal line = 91°)

	1	2	3	4	5	6	7	8	9
Surface 1:	53-30	156-30	60	26	124	106-30	124	116	110
Surface 3:	141	11-30	73-30	73-30	122	106-30	64-30	67-30	73-30
	10	11	12	13	14	15	16	17	18
Surface 1:	68	57	62-30	116-30	91-30	110	58	27-30	125-30
Surface 3:	141-30	138-30	97	76-30	165	73-30	72-30	99	62
	19	20	21						
Surface 1:	102-30	49	131						
Surface 3:	99-30	140	120						

*Fifth Operation* (Angle of edge with basal line = 2°)

	1	2	3	4	5	6	7	8	9
Surface 1:	100	139	108	105-30	57	52	137-30	31-30	53-30
Surface 2:	105-30	103-30	48-30	101-30	82	72	41	131	79
	10	11	12	13	14	15	16	17	
Surface 1:	138-30	112	110	106	111	112	41-30	33	
Surface 2:	104-30	94-30	101	122	139-30	103-30	124-30	130	

*Sixth Operation* (Angle of edge with basal line = 91°)

	1	2	3	4	5	6	7	8	9	10	11
Surface 1:	149	113	19	115	139	110	124	117	119	23	91
Surface 3:	97	67	62	68-30	122	73-30	119	68	120	156-30	156-30
	12	13	14	15	16						
Surface 1:	42	53-30	43	101-30	45-30						
Surface 3:	82	138	81	91	118-30						

*Seventh Operation* (Angle of edge with basal line = 2°)

	1	2	3	4	5	6	7	8
Surface 1:	99	141-30	114-30	140	94-30	139	57	59-30
Surface 2:	45-30	148	94-30	118	135	148	89	26

*Eighth Operation* (Angle of edge with basal line = 91°)

	1	2	3	4	5	6	7	8	9	10
Surface 1:	158	23	157	108	104	56-30	43	99-30	50	41
Surface 3:	10-30	154	12	72	98	72-30	86	115-30	75-30	84
	11	12	13	14	15	16				
Surface 1:	51	41	90	10	144	69-30				
Surface 3:	81	84	153	179	117	142				



of the straight line and great circle for each cementite plate traced around the edge defined the stereographic projection of that plate. The result of the stereographic plot of the 103 cementite plates listed in Table 2 is given in Fig. 12.

Inspection of this projection shows immediately that all points group themselves in three circles of which the centers are  $90^\circ$  apart. (The half circle in the upper right-hand quadrant is a continuation of that in the

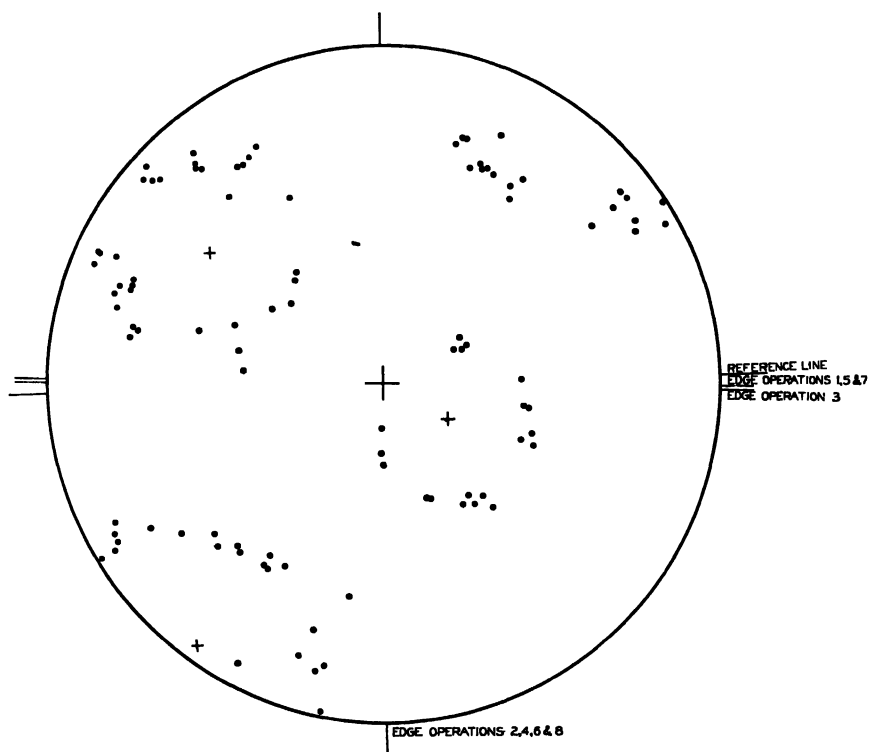


FIG. 12.—STEREOGRAPHIC PROJECTION OF ORIENTATIONS OF CEMENTITE PLATES.

lower left-hand quadrant.) The suggestion is therefore strong that these points are grouped about the three  $\{100\}$  poles. Proceeding on this basis, circles were drawn through the points on each of the three circles to represent the average positions and the centers of gravity of the small circles approximated by taking the average point of intersection of great circle diameters. These points were then rotated to standard  $\{100\}$  positions, and found to coincide with the  $\{100\}$  poles with surprising accuracy. Accordingly all of the 103 points were then rotated into the same standard projection (Fig. 13), and finally—in order more readily to study the grouping of these points—into one corner of one quadrant (Fig. 14).

Fig. 14 thus represents the results of the eight operations. It will be seen immediately that there is considerable scattering, though the points with a few exceptions lie approximately on a stereographic circle around (100), also shown in Fig. 14, and tend roughly to arrange themselves into three groups. This scattering makes it impossible to determine exactly the planes in the austenite to which the cementite plates are parallel. In order to obtain an idea of the approximate indices of these

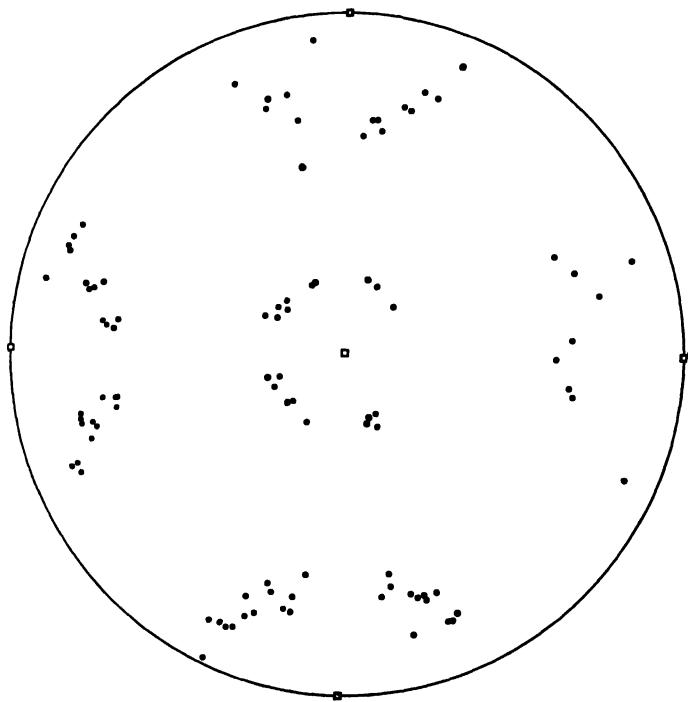


FIG. 13.—STEREOGRAPHIC PROJECTION OF ORIENTATIONS OF CEMENTITE PLATES ROTATED INTO A STANDARD POSITION.

planes, Fig. 15 was prepared, a standard projection giving the planes lying in the neighborhood of the experimental points; for ready comparison, the small stereographic circle shown in Fig. 15 is included in this diagram.

Although it is impossible to determine the planes of precipitation in the austenite phase, it might be pointed out that (512) and (521) are near the centers of gravity of the two outside groups and that (722) is near to that of the middle group.

The scattering of these points is not surprising in view of the fine structure of the plate shown in Figs. 6 to 9. It is possible that the several points that fall far from the main groups may have been taken from plates with false directions, such as that shown in Fig. 8, but since the microscopic study of the plates was undertaken after the analysis of their

orientation, and indeed in an endeavor to explain the scattering observed, it was impossible to attempt to confirm this possibility.

The scattering of the points, exclusive of those falling far from the main groups, is much greater than usually observed in Widmanstätten figures, a condition probably engendered by the distortion effects producing the corrugations observed in the plates.<sup>32</sup>

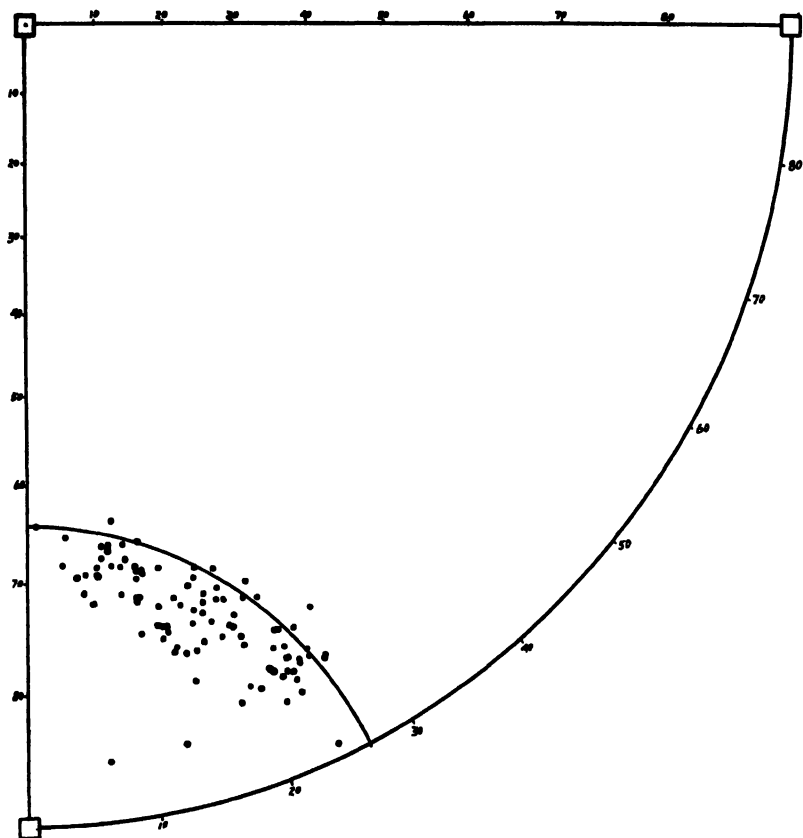


FIG. 14.—STEREOGRAPHIC PROJECTION OF ORIENTATIONS OF CEMENTITE PLATES ROTATED INTO ONE CORNER OF A QUADRANT.

*Determination of Orientation of Cementite Plates.*—A complete solution of this problem requires a determination of the plane in the cementite lattice parallel to the plane of the cementite plate, and also a determination of the exact position or positions taken by this plane of atoms with respect to the plane of atoms in the austenite along which the plate forms.

<sup>32</sup> It is quite possible that an analysis of the orientation of proeutectoid cementite in manganese or other inherently austenitic steels, in which the distorting effects of the volume change at the eutectoid inversion may be avoided, would be more successful than that reported here. The authors hope shortly to attempt this.

This second determination of the complete solution was not obtained; the first, however, was successfully performed. Although the solution is accordingly incomplete, some interesting inferences may be drawn from the data.

Cementite plates were separated from the pearlite matrix in a specimen similar to that shown in Fig. 11, by electrolytic dissolution. Two such plates—approximately 0.5 mm. in diameter and 0.01 mm. thick—

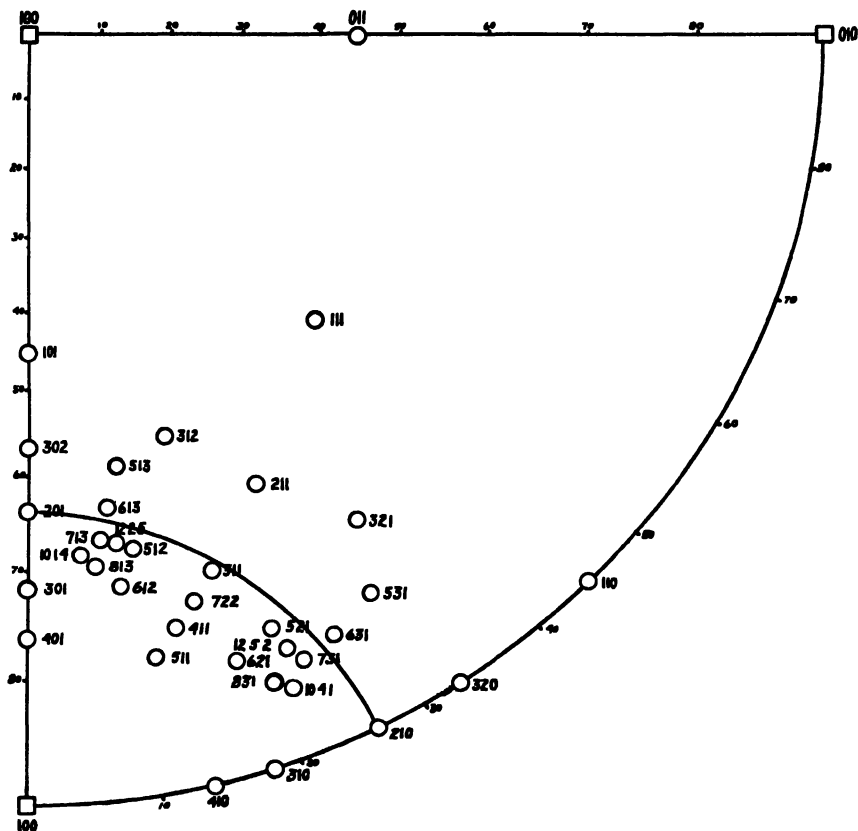


FIG. 15.—STEREOGRAPHIC PROJECTION OF ATOM PLANES NEAR CEMENTITE GROUP.

were mounted on celluloid and cemented in place by a dilute alcoholic solution of shellac. One of these plates is shown in Fig. 9. Laue photographs were then taken of each plate using Mo characteristic radiation (30,000 volts, 18 milliamperes) impinging normally upon the cementite plate, with a distance of specimen to photographic plate of 4 cm. and an exposure time of 96 hours.

The photographs obtained from the two cementite plates were very similar; one of the patterns obtained is shown in Fig. 16. The symmetry

of the spots in this photogram appears typical for irradiation of a single crystal parallel to one of the principle axes, but efforts to assign indices by the use of a gnomonic projection were entirely unsuccessful.

Photograms taken with white W radiation (30,000 volts, 24 milliamperes) were entirely different in appearance (Fig. 17). Instead of

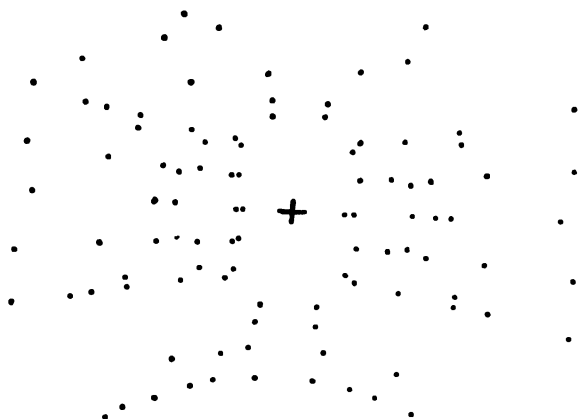


FIG. 16.—TRACING OF LAUE PHOTOGRAM OF CEMENTITE PLATE, Mo RADIATION

sharply defined spots, only radial streaks were obtained, proving quite definitely that the specimens were not perfect single crystals but either bent crystals or aggregates of small crystals of nearly identical orientation. The well-known brittleness of cementite would appear to eliminate the

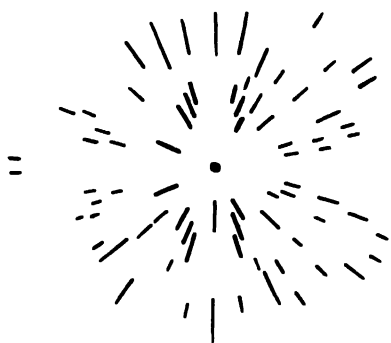


FIG. 17.—TRACING OF LAUE PHOTOGRAM OF CEMENTITE PLATE, W RADIATION.

possibility of elastic bending and to leave the alternative of an aggregate of small crystals of nearly identical orientation. It was found that the Mo photograms could be considered as "layer-line" photograms, subject to standard methods of analysis.

The details of analysis are given in Appendix A, and we shall note here only the results: the two  $\text{Fe}_3\text{C}$  plates separated from the pearlite matrix were not each a single crystal, but a fragmented crystal.

These fragmented crystals each possessed a (fragmented and discontinuous) (001) plane—the basal plane of the cementite lattice in Fig. 10—approximately parallel to the face of the plates. The warping or fragmentation of the crystals was found to be such that all [100] directions were parallel but that [010] directions varied between  $0^\circ$  and approximately  $10^\circ$  on each side of the  $\text{Fe}_3\text{C}$  plate. This X-ray evidence of frag-

mentation is in confirmation of the micrographic evidence in Figs. 6, 7, 8 and 9. However, the preferred type of fragmentation observed (limited fibering with the [100] direction as fibering axis) is puzzling. Perhaps the [100] direction in cementite lies in an important cleavage plane along which the crystal fractured during cooling.

*Relationships in Orientation between Austenite Lattice and Cementite Plate.*—Since the observations on the orientations of  $\text{Fe}_3\text{C}$  plates with respect to austenite do not allow an exact choice of the austenite planes to which the  $\text{Fe}_3\text{C}$  plates lie parallel, an extended discussion of possible atom movements would hardly be warranted. Certain lattice relationships, however, should be pointed out.

If the assumption is made that the observed warping of the cementite plates occurred subsequent to their formation and not during their genesis by some obscure growth mechanism, it follows that the conjugate plane in cementite should be taken as the basal (001) plane.

Projections of the atoms in the  $\text{Fe}_3\text{C}$  lattice upon the basal plane have accordingly been prepared and compared with projections of the atoms in the austenite lattice upon various planes. The projections of the atoms in the austenite lattice were prepared by the method given in Appendix B.<sup>33</sup>

No atom planes in the austenite lattice were found that have an extensive similarity to the distribution of iron atoms upon the (001) plane of  $\text{Fe}_3\text{C}$ . There is however an agreement in atom spacing along the [112] direction in the austenite lattice and the [100] direction (which lies in the basal (001) plane) in the  $\text{Fe}_3\text{C}$  lattice; the interatomic distances along these directions are 4.43 Å for [112] $\gamma$  and 4.52 Å for [100] $\text{Fe}_3\text{C}$ , a difference of only 2 per cent.

The {311} planes in austenite each contain two [112] directions. A projection of the austenite atoms upon this plane (Fig. 18a and b) shows an interesting and rather unusual type of coincidence with the projection of the  $\text{Fe}_3\text{C}$  iron atoms upon the (001)  $\text{Fe}_3\text{C}$  plane (Fig. 18c and d).

The atoms in these two figures may be made to coincide quite closely by simple superimposition, but only within a strip. Along the [112] $\gamma$  and [100] $\text{Fe}_3\text{C}$  directions the coincidence extends for a considerable distance, but normal to this the atoms quickly fall out of coincidence. This coincidence extends to a depth of four atom layers; the interplanar distances in the two lattices are nearly equal, for the {311} $\gamma$  this is 1.09 Å, which differs by only 3 per cent from the average interplanar distance for the (001)  $\text{Fe}_3\text{C}$  planes, 1.12 Å.

This type of matching can hardly be advanced as a reason for the widely varying orientations shown in Fig. 14, yet it is an interesting fact

<sup>33</sup> Many such projections of the austenite lattice were made, including projections upon the planes (111), (211), (311), (411), (522), (722), (731), (521), (210). All projections were made for Fe atoms only, since the interstitial C atom distributed at random in austenite can hardly play a major part in the crystallographic mechanism.

that the observed fragmentation of the  $\text{Fe}_3\text{C}$  plates and the striations upon the surface of the  $\text{Fe}_3\text{C}$  plates are along the  $[100]$   $\text{Fe}_3\text{C}$  direction. The direction in the austenite lattice lying parallel to this direction was not determined, and accordingly the argument cannot be carried further.

### Structures Formed on Quenching

*Hypoeutectoid, Eutectoid, and Hypereutectoid Alloys.*—We shall restrict ourselves here to a study of only the planes delineated by the martensitic

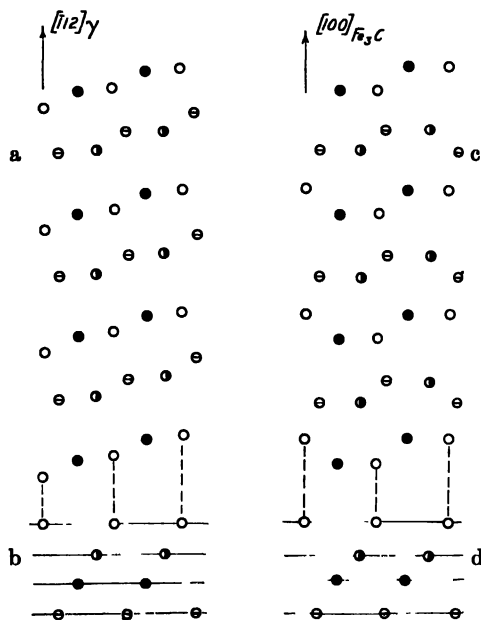


FIG. 18—*a*. PROJECTION OF IRON ATOMS IN AUSTENITE UPON (311) PLANE. *b*. ELEVATION, SHOWING SEQUENCE OF (311) PLANES AND THEIR SPACING. *c*. PROJECTION OF IRON ATOMS IN CEMENTITE UPON (001) PLANE OF CEMENTITE. *d*. ELEVATION, SHOWING SEQUENCE AND SPACING OF FOUR (001) PLANES

“needles” in alloys of varying carbon content, since, as we shall note, a complete solution to the problem has been furnished by Kurdjumow and Sachs (ref. 3) for a hypereutectoid steel with 1.4 per cent C. and since in all probability the crystallographic mechanism of the formation of martensite in low-carbon steels is the same as that in high-carbon. The results of Kurdjumow and Sachs had been largely anticipated by Jeffries, but we shall restrict ourselves to the work of the former because of its completeness.<sup>34</sup>

<sup>34</sup> Zay Jeffries prepared X-ray photographs of martensite and showed that the multiplicity in orientation of the ferrite observed could not be accounted for by the simple type of transformation mechanism previously postulated by E. C. Bain [Nature of Martensite. *Trans. A. I. M. E.* (1924) **70**, 25–46], and also indicated the

*Determination of Plane Demarked by Martensite "Needle."*—The close similarity in structural appearance between the martensitic structures in steel and the Widmanstätten figure in meteorites had led a number of authors, notably Sauveur,<sup>35</sup> to assume that the martensitic "needle" delineates the octahedral plane in the parent austenite as kamacite is known to delineate the octahedral plane in the parent taenite. So far as the authors are aware, however, no careful study of this point has been made, particularly with reference to the whole range of carbon contents represented in austenite.

For this purpose, three steels were chosen, a hypoeutectoid steel with 0.42 per cent C (S.A.E. 1040), a eutectoid steel with 0.86 per cent C (a simple carbon tool steel), and a hypereutectoid steel with 1.3 per cent C (one of the cast ingots used above). Each of these was heated at 1100°C. for 2 hr., quenched in water at room temperature, reheated to 200°C. for 1 hr., and then prepared for microscopic examination.

Since the orientation of the original austenite could not easily be determined (it might be noted here that Kurdjumow and Sachs were able to determine the orientation of the austenite), the study was restricted to a simple count of the directions taken on the surface of polish by the mid-ribs of the martensite "needles." As noted previously in this series of papers, such a method is adequate for the determination of a plane when its indices are low. An average of 70 needles was measured in each individual austenite cell, and 12 such cells were studied in each of the three steels. Fig. 19 shows the results of these measurements, giving the results of four of each of the 12 austenite cells in each of the steels in the form of frequency curves; 1 to 4 represent the hypoeutectoid steel, 5 to 8 the eutectoid, and 9 to 12 the hypereutectoid. It is a general (and well recognized) fact that the sharpness of definition of the martensitic structure increases with increasing carbon content and thus the distinctness of the "needle" direction in the hypoeutectoid alloy was inferior to that in the other two alloys, though adequate for the present purpose.

It may be seen from these frequency curves that the angular positions of the "needles" scatter considerably. This is to be expected, for the shock of quenching and the volume change accompanying the austenite-martensite transformation must introduce a complex of severe internal strains in the transforming austenite, resulting in a violent disturbance of lattice planes and transformation products. Nevertheless, it is clear from

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(111) $\gamma$  - (110) $\alpha$  plane transformation with the resultant multiplicity of ferrite orientations, though he did not analyze the X-ray photograms [A Contribution to the Theory of Hardening and the Constitution of Steel. *Trans. Amer. Soc. Steel Treat.* (1928) **13**, 369-405].

<sup>35</sup> A. Sauveur: The Widmanstätten Structure of Iron Alloys *Proc. Amer. Phil. Soc.* (1927) **66**, 267; Austenite and Its Decomposition. *Trans. Amer. Soc. Steel Treat.* (1930) **17**, 199.



Fig. 19, and from the remaining frequency curves not shown, that a maximum of four directions is exhibited in each of the three steels, which

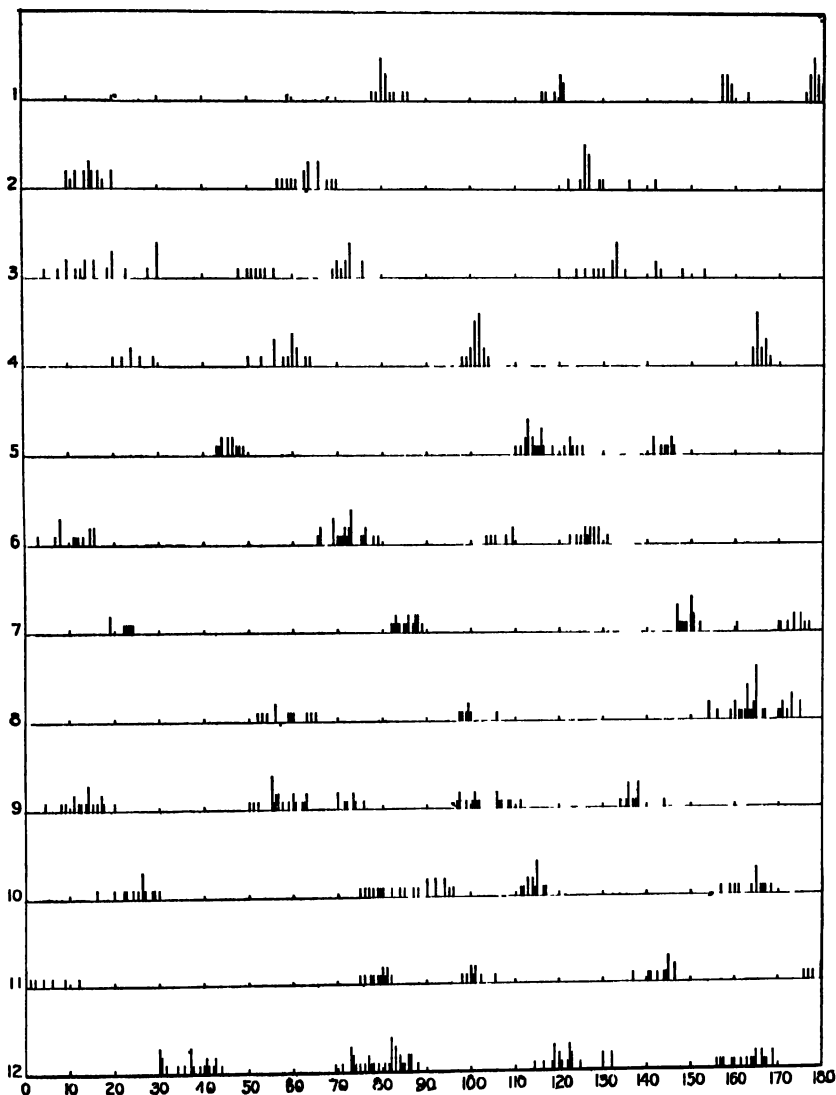


FIG. 19.—FREQUENCY PLOTS FOR ORIENTATION OF TRACES OF MARTENSITE "NEEDLES" UPON A SURFACE OF POLISH.

Plots 1- 4, hypo-eutectoid alloy.

Plots 5- 8, eutectoid alloy

Plots 9-12, hyper-eutectoid alloy.

may be taken as sufficient proof that the martensitic structure delineates the octahedral plane in the parent austenite, regardless of carbon content.

*Orientation of Ferrite with Respect to Parent Austenite.*—Although no work on this subject has been done by the present authors, for the sake of completeness the work of Kurdjumow and Sachs should be briefly recorded here

By preparing a large crystal of austenite and subsequent rapid quenching Kurdjumow and Sachs obtained a sample, martensitic in appearance under the microscope, but containing considerable residual austenite. The occurrence of residual austenite made possible a determination of orientation of the original austenite by proper face-pole figure analysis of spots on X-ray photograms. With this determined, the orientation of the tetragonal lattice present in the freshly quenched piece, and of the body-centered cubic ferrite formed by heating, could be determined in like manner.

We need concern ourselves here only with the analytical result. In all probability the body-centered tetragonal lattice is a supersaturated solution of carbon in  $\alpha$  Fe, preserved in some semblance of stability by the distending effect of the interstitial carbon atoms retained from the austenite. Upon rejecting this carbon—with time or upon heating—the tetragonal lattice alters its dimensions to that of  $\alpha$  Fe (Fig. 1b). The result of the transformations of austenite to the body-centered tetragonal and to the body-centered cubic lattices was found by Kurdjumow and Sachs to be that indicated in the early part of this paper; in either event the mutual orientation is of the type  $(111)\gamma$  parallel to  $(011)\alpha$  and  $[\bar{1}\bar{1}0]\gamma$  parallel to  $[11\bar{1}]\alpha$ , resulting in six orientations of the transformation products upon each octahedral plane of the austenite, or a total of 24 orientations. All of these were found.

This transformation, then, is entirely analogous to the crystallographic transformation taking place upon the precipitation of ferrite on the slow cooling of hypoeutectoid alloys, as shown above.

It might be remarked that though Kurdjumow and Sachs studied only a 1.4 per cent C steel, the similarity in martensitic structures for the whole range of carbon contents, as reported in the first part of this section and as generally recognized, is a strong indication if not direct proof that the transformation in lower carbon steels is of the same type.

#### DISCUSSION OF RESULTS

From the point of view of the theory for the formation of Widmanstätten figures, the results given here are in corroboration of previous results. As in the work on the  $\beta$  Cu-Zn alloys (ref. 2), we find that the lattice type of the parent solid solution is not the only factor in determining the type of Widmanstätten figure formed, for in slowly cooled hypoeutectoid alloys ferrite precipitates from austenite in plates parallel to the  $\{111\}$  planes in austenite, whereas hypereutectoid alloys precipitate cementite parallel to some plane or planes near to  $\{521\}$  and  $\{722\}$ ;

definitely not on the  $\{111\}$  planes. We again are forced to conclude that the crystal structure of the precipitate is also of primary importance in determining the position and orientation of the precipitate.

The formation of ferrite in hypoeutectoid alloys proceeds by a mechanism doubtless inherent in the  $\gamma$ - $\alpha$  transformation in pure iron; except in determining the rate of formation—by the necessity for adequate diffusion—the carbon therefore plays an unimportant part. We may suspect that this also happens in the precipitation of  $\text{Fe}_3\text{C}$ , though the lack of a complete analysis at the present moment does not justify a definite statement.

With these points in mind, the transformation in quenched alloys becomes particularly interesting. Throughout the range of carbon concentration in austenite, the crystallographic mechanism remains essentially the same and identical with that for slowly cooled hypoeutectoid alloys and with that which may be confidently assumed for the  $\gamma$ - $\alpha$  transformation in pure iron. In other words, the factor that determines the crystallographic structure of martensite is that inherent in the  $\gamma$ - $\alpha$  change.

We may also note that the results given here, and those previously given by Young for meteorites and by Kurdjumow and Sachs for quenched steels, show that a number of orientations of precipitate may occur upon one plane in the parent solid solution lattice. This number is determined by crystallographic similarities along directions in the two participating lattices, and its multiplicity may be predicted by the possible combinations of equivalent and conjugate directions.

Howe (refs. 7 and 22) has shown that ferrite precipitates more rapidly from austenite than does cementite. Similar results have been obtained in this laboratory by the use of the dilatometer. Although there are several factors that must determine rates of precipitation, it is probable that similarity in atomic spacing and symmetry in the participating phases is an important factor, particularly with respect to the establishment of nuclei but also probably with respect to subsequent growth. The similarities existing between the ferrite and austenite lattices, and relative lack of similarities between the cementite and austenite lattices, might well be taken as one factor determining the ease of formation of ferrite nuclei and the difficulty of formation of cementite nuclei, and eventually the relative rapidity of ferrite precipitation and sluggishness of cementite precipitation. We may propose, then, that the absence of lattice similarities between a parent solid solution and a precipitating phase may be an important factor in determining the ease of supersaturation or undercooling.

#### SUMMARY

1. The structure of Widmanstätten figures in slowly cooled hypoeutectoid and hypereutectoid, and in quenched (martensitic) hypoeutectoid, eutectoid, and hypereutectoid Fe-C alloys has been studied.

2. The orientation of proeutectoid ferrite in slowly cooled hypoeutectoid Fe-C alloys has been completely demonstrated. Upon each of the four (111) planes in austenite ferrite forms in plates of six distinct orientations, resulting in a total of 24 ferrite orientations from each austenite grain.

3. Proeutectoid cementite in slowly cooled hypereutectoid alloys is in the form of laminated and distorted plates, parallel to planes in the austenite of high indices definitely not  $\{111\}\gamma$ . Several possible  $\{hkl\}\gamma$  planes have been suggested. The basal plane (001) of the  $\text{Fe}_3\text{C}$  lattice forms approximately parallel to the plane of the  $\text{Fe}_3\text{C}$  plate, with a deviation of several degrees of the type of limited fibering with the  $[100]\text{Fe}_3\text{C}$  axis as the fibering axis.

4. The plane in austenite delineated by the martensitic structure is the  $\{111\}$  in hypoeutectoid, eutectoid and hypereutectoid Fe-C alloys. The basic crystallographic process obtaining in the formation of martensite is essentially that inherent in the  $\gamma \rightarrow \alpha$  change in pure iron, as is also the mechanism of the proeutectoid rejection of ferrite.

5. The results of this work are in confirmation of the theories for the formation of Widmanstätten figures previously proposed in this series of papers.

#### ACKNOWLEDGMENT

The steels used in this work were prepared and furnished to us by Mr. P. E. McKinney, of the Bethlehem Steel Co.; without this assistance it would have been very difficult to accomplish the work. Prof. L. W. McKeehan, of Yale University, lent us timely aid in suggesting fibering in the  $\text{Fe}_3\text{C}$  plates as a reason for the unusual type of Laue photographs obtained.

Much of this work was done at the Naval Research Laboratory in Washington, D. C.; we wish particularly to acknowledge the interest and sympathy of the Director of that laboratory, Commander E. D. Almy, U. S. N.

#### APPENDIX A.—ORIENTATION OF AN $\text{Fe}_3\text{C}$ PLATE

The photograph of an  $\text{Fe}_3\text{C}$  plate with molybdenum radiation (unfiltered) was analyzed as an oscillating crystal photograph, using graphic methods and the reciprocal lattice concept.<sup>36</sup>

The first step was to determine the crystallographic axis or axes about which the warping or bending occurred in the plate. To do this the film was enlarged to a size corresponding to a specimen-film distance of 10 cm. and superimposed upon a chart for rotation photograph interpreta-

<sup>36</sup> J. D. Bernal: On the Interpretation of X-ray Single Crystal Rotation Photographs. *Proc. Roy. Soc.* (1926) **113**, 117-160.

tion.<sup>37</sup> It was at once apparent that rotation was about a single axis, because the spots lay on well defined layer lines.

By means of the chart the coordinates  $\zeta$  and  $\xi$  of each spot were read and the Miller indices ( $hkl$ ) of each reflecting plane determined from these coordinates by the relations:

$$\zeta = \frac{h\lambda}{a} \text{ and } \xi = \sqrt{\frac{k^2\lambda^2}{b^2} + \frac{l\lambda^2}{c^2}}$$

where  $a$ ,  $b$  and  $c$  are the identity periods along the orthorhombic axes.

In Table 3 the first column is the value of  $\zeta$  for every layer line observed due to both  $\text{MoK}_\alpha$  and  $\text{MoK}_\beta$  rays; the second column the values of  $h\lambda$  assumed to account for them, and the third column the identity period of the lattice in the direction of the assumed axis.

TABLE 3

$\zeta$	$h\lambda$	$\frac{h\lambda}{\zeta}a$	$\zeta$	$h\lambda$	$\frac{h\lambda}{\zeta}a$
0 143	0.631	4 42	0 482	3x 710	4 42
0 159	0 710	4 46	0 562	4x 631	4 49
0 282	2x 631	4 48	0 635	4x 710	4 47
0 319	2x 710	4 45			
0 425	3x 631	4 46		Mean	4 46

The values of  $h\lambda/\zeta$  deviated from the mean by no great amount, and the mean differed by but 1.3 per cent from the period along the shortest side,  $a$ , of the unit cell of  $\text{Fe}_3\text{C}$ , while it differed 13.6 per cent from the  $b$  dimension and 50.7 per cent from the  $c$  dimension. From the work that follows it seems clear that the 1.3 per cent discrepancy was caused simply by experimental error in setting the crystal and film and in enlarging.

It was therefore assumed that the pattern was a rotation photograph of a crystal of apparent lattice dimensions:

$$\begin{aligned} a &= 0.9878 \times 4.518 = 4.46 \\ b &= 5.069 \times 0.9878 = 5.005 \\ c &= 6.736 \times 0.9878 = 6.650 \end{aligned}$$

with rotation about  $a$ . The Miller index  $h$  having been thus assigned to every spot, the indices  $k$  and  $l$  were given all possible small integral values except those corresponding to planes in  $\text{Fe}_3\text{C}$ , which do not reflect.

Table 4 lists the spots: in column 1 are given the possible indices, in column 2 the calculated  $\xi$  values corresponding to these indices and in column 3 the observed  $\xi$  values. It was found that every spot could be assigned indices from planes known to reflect in the  $\text{Fe}_3\text{C}$  lattice. The

<sup>37</sup> Chart No. 1 by J. D. Bernal (*loc. cit.*), on which are plotted lines for constant values of  $\zeta$  and of  $\xi$ .

calculated and observed  $\xi$  values are not included in the table but were satisfactory in every case; their order of accuracy is seen from Table 1.

TABLE 4

Possible Index ( <i>hkl</i> )	Calculated $\xi$	Observed $\xi$	$\eta$ (Degrees)
311	0 177	0 18	11
412	0 256	0 26	8
020	0 284	0 28	8
021	0 303	0 31	11
121	0 303	0 30	9
221	0 303	0 30	1
422	0 355	0 37	10
131	0 439	0 44	1
{ 432 or	0 428 }	0 43	6
{ 431	0 439 }		(27)
232	0 476	0 48	6
332	0 476	0 48	3
433	0 534	0 53	3
141	0 577	0 58	8
{ 025 or	0 604 }	0 60	(39)
{ 042	0 622 }		3
043	0 652	0 65	10
{ 206 or	0 641 }		(65)
{ 243 or	0 652 }	0 65	6
{ 216	0 658 }		(52)
{ 152	0 741 }	0 73	6
{ 107	0 747 }		(67)
252	0 741	0 74	10
{ 245 or	0 779 }		(16)
{ 236 or	0 769 }	0 77	(29)
{ 253	0 778 }		3

Every spot on the photograph, therefore, is explicable on the basis that the cementite plate, mounted perpendicular to the X-ray beam, had its [100] direction in the plane of the plate and was fragmented or imperfectly grown in such a manner that the [100] direction of all portions—but not the [010] or [001] directions—were parallel. The diffraction effect was similar to a rotation photograph made by rotating a single crystal about the [100] axis.

The limits of this "rotation" were determined as the limits of variation from a zero position defined as that in which the basal plane (001) is normal to the primary X-ray beam. The angle of variation,  $\eta^\circ$ , was calculated for each spot; the maximum value for  $\eta^\circ$  is thus the maximum variation from the zero position found, with some qualification as noted below. The method of calculation used was a graphic one, using a pro-

jection of the reciprocal lattice.<sup>38</sup> The results are given in the last column of Table 2.

Most of the  $\eta$  values were less than  $11^\circ$ . Every spot for which a possible index existed with  $\eta$  greater than  $11^\circ$  also had a possible index for which  $\eta$  was less than  $11^\circ$ . (These values of  $\eta$  are inclosed in parentheses in the table.) In almost every case reflections occurred four times for each plane of form  $(hkl)$ ; *i. e.*, on both right and left sides of the  $a$  axis and both above and below the  $b$  axis. The exceptions to this are the (021), (252) and (043) reflections. Each of these was at the limit of oscillation, reflecting at  $\eta = 10^\circ$  or  $11^\circ$  so they serve accurately to define the limit of oscillation. The (252) reflection occurred in both the lower right and lower left quadrants but not in the upper right or upper left, showing that the angles between the X-ray beam and the  $a$  axis was not exactly  $90^\circ$ .

Accordingly, we may say that the plate studied was not a single crystal, but a composite of crystallites with the  $a$  axes all parallel, and with the basal plane (001) approximately in the surface of the plate but varying from this position from crystal to crystal through an angle of  $\pm 10^\circ$ . The uniform distribution of intensity in the interference striae of the tungsten Laue photogram indicates a large number of individual crystallites and an approximate uniform distribution of crystallites throughout the observed angular range.

#### APPENDIX B.—PLOTING OF ATOMS ON THE $(hkl)$ PLANE OF A CUBIC LATTICE

The plot of atoms on any given plane in a cubic lattice, and the projection of neighboring atoms on this plane, may be conveniently obtained in the following manner.

Let the coordinates of an atom referred to the axes  $X, Y, Z$  of the cubic lattice be  $x, y, z$ . Let  $X', Y', Z'$  be another set of mutually perpendicular axes, with their origin coinciding with the first, so chosen that  $X'$  and  $Y'$  lie in the desired projection plane; and let the required coordinates of the atom when referred to the new set of axes be  $x', y', z'$ . When the coordinate  $z'$  of an atom is zero the atom lies upon the chosen projection plane passing through the origin, and  $x'$  and  $y'$  are the coordinates of the atom on this plane; when  $z'$  is not equal to zero its value is the distance of the atom from this plane and  $x'$  and  $y'$  are the coordinates of the projection of the atom on this plane. Equal values of  $z'$  occur for all atoms on a single plane.

Referred to  $X, Y, Z$ , let the direction cosines of  $X'$  be  $l_1, m_1, n_1$ ; the direction cosines of  $Y'$  be  $l_2, m_2, n_2$ , and the direction cosines of  $Z'$  be

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<sup>38</sup> Cf. Bernal, footnote 36.

$l_3, m_3, n_3$ . The new coordinates of the atom will then be given by the formulas

$$\begin{aligned}x' &= l_1x + m_1y + n_1z \\y' &= l_2x + m_2y + n_2z \\z' &= l_3x + m_3y + n_3z\end{aligned}\quad [1]$$

The required direction cosines in these equations are readily calculated from the Miller indices of the new axes, for if the Miller indices of one of the new axes are  $[HKL]$  the direction cosines of this new axis will be

$$l = \frac{H}{\sqrt{H^2 + K^2 + L^2}}, m = \frac{K}{\sqrt{H^2 + K^2 + L^2}}, n = \frac{L}{\sqrt{H^2 + K^2 + L^2}} \quad [2]$$

Thus, given the Miller indices of the new coordinate axes, their direction cosines may be calculated by formulas 2; these direction cosines may then be introduced in formulas 1 together with the coordinates of the atom in question derived from the old set of coordinate axes, and the coordinates of the atom in question with respect to the new set of coordinate axes calculated.

For example, in plotting the (311) plane of austenite new axes were chosen as follows:  $Z'$  was chosen normal to the (311) plane and thus had indices  $[311]$ ; the intersection of the (311) and (100) planes was taken as  $Y'$  which therefore had indices  $[01\bar{1}]$ ; and  $X'$ , since it was perpendicular to  $[311]$  and  $[01\bar{1}]$  had indices  $[23\bar{3}]$ . The above equations for transformation of coordinates then become

$$\begin{aligned}x' &= \frac{2}{\sqrt{22}}x - \frac{3}{\sqrt{22}}y - \frac{3}{\sqrt{22}}z \\y' &= \frac{1}{\sqrt{2}}y - \frac{1}{\sqrt{2}}z \\z' &= \frac{3}{\sqrt{11}}x + \frac{1}{\sqrt{11}}y + \frac{1}{\sqrt{11}}z\end{aligned}$$

Substitution of the atom coordinates  $x, y, z$  will then give the desired atom coordinates. Thus the atom of coordinates 1, 1, 1 with respect to the old system of coordinate axes will have the coordinates  $-\frac{4}{\sqrt{22}}, 0,$

$\frac{5}{\sqrt{11}}$  with respect to the new. Note that the choice of new axes is made in a specific order: the first axis is placed normal to the chosen plane, the second axis is taken arbitrarily in the chosen plane in some convenient direction, and the third axis is taken normal to the first and second. The choice of the second and third axes, necessarily perpendicular for the purposes of the method, may be made by the use of the formula  $HH' + KK' + LL' = 0$  which is the general expression for two axes at right angles of indices  $[HKL]$  and  $[H'K'L']$  at right angles to each other.



## DISCUSSION

(W. P. Sykes presiding)

A. SAUVEUR, Cambridge, Mass.—It is always pleasant to have one's predictions and the conclusions of one's own work confirmed by the results obtained by others. Had the authors of this paper, however, reached conclusions contrary to mine, my admiration for their method, skill and soundness of argumentation would not have been less.

As they have stated, I had predicted that the allotropic transformation of  $\gamma$  iron into  $\alpha$  iron should take place gradually, although possibly very quickly, through the new  $\alpha$  phase forming around the boundaries of the austenite grains and along some crystallographic planes giving rise during the process of transformation to Widmanstätten type of structure. Later, with the assistance of Dr Chou, I was able to show that such indeed was the case.

In subsequent publications I offered evidence to show that in a hypoeutectoid steel when slowly cooled, resulting in pearlitic structure or quickly resulting in martensitic structure, the mechanism of the decomposition of austenite was substantially the same, again yielding Widmanstätten structures. I inferred, reasonably I think, that in hypereutectoid steel, cementite would likewise locate itself around the boundaries and along the (111) planes. The authors show conclusively that such is not the case; that cementite forms along other crystallographic planes than (111) planes and this constitutes a distinct addition to our knowledge.

It would be difficult not to agree with the authors in their belief that the crystal structure of the precipitate is also of importance in determining its position and orientation and likewise with their thought that the degree of lattice similarity between the solvent and precipitate may be an important factor in the ease with which supersaturated solutions may be obtained.

N. T. BELAIEW, Paris, France (written discussion).—The characteristic "geometric" figures on meteorites were observed first in 1808 by Alois de Widmanstätten, the Director of the Imperial Porcelain Works at Vienna, on the Hradschina meteorite. Although Widmanstätten himself did not publish anything about his discovery, the knowledge spread very quickly and soon what he had seen was known as "Widmanstätten figures." For a considerable time it was considered that these figures were characteristic of meteoric iron and that they were not found in terrestrial alloys.

It was only in 1900 that Osmond announced the discovery of equilateral triangles in the head of a steel ingot, which recalled, he said, "the figures of Widmanstätten, which are known to belong to the octahedral system." At the Royal Society's Conversation in London, in May, 1903, microscopical preparations of meteoric and artificial irons were shown by Dr. Stead; by applying Widmanstätten's method of "heat-tinting" he was able "to produce a minute structure of a piece of artificial iron in which small but beautifully marked Widmanstätten figures had been developed by the very slow cooling of the mass from a high temperature."<sup>39</sup> The same observation was made in 1905 by Arnold and McWilliam.<sup>40</sup> These observations did not become widely known then, and when some two years later I started my work on the crystallization of steel, I was ignorant of them and still under the impression that Widmanstätten figures were met with only in meteorites.

About twenty alloys were prepared under conditions of slow and undisturbed cooling, following the directions of my teacher, Prof. D. K. Tschernoff, for the prepara-

<sup>39</sup> *Min. Mag.* (1903) 13, 304.

<sup>40</sup> *Jnl. Iron & Steel Inst.* (1905) 68, 35.

tion of Damascene steel and well developed macrostructures in general. The first series was prepared in the spring of 1907 at the Putilov works, and showed beautiful primary and secondary crystallization. In order to test the results, another works, this time the Ijevsky steel foundry in the Urals, was asked to repeat the experiment and to let me have samples of crucible steel slowly cooled in the crucibles. This time a real puzzle was offered by the structure of the specimen No. 8, with 0.55 per cent C, which instead of a net structure, like the one of the corresponding alloys 5 and 6, seemed at first to consist of parallel running white stripes. It was considerable time before we realized that the band structure was but accidental, and that the various "geometric" figures subsequently revealed were actual Widmanstätten figures, and this time not in a meteorite, but in a terrestrial alloy.

Correspondence with Osmond, Howe, Sauveur, Benedicks and Berwerth revealed the interest that metallurgists and mineralogists paid to these figures, and subsequent research showed that these figures, together with the corresponding network, had to be considered as a definite secondary structure, and together with the more usual network structure and the structure of large crystals formed a triad of secondary structures. On this ground, and in honor of Widmanstätten, the name of Widmanstätten structure was proposed for this secondary structure and eventually adopted by metallographers.

First, the genesis of the Widmanstätten structure seemed to be the more actual problem, but subsequently the crystallographic aspect of the question became apparent, as it became clear that by counting the number of directions the crystallographic indices of the major sections can be brought into evidence. This side of the question was particularly emphasized by Professor Sauveur. Another aspect of the question was the relation between the orientation of various adjacent grains; to study it the orientation of every grain in space had to be determined; this was done in 1923 in collaboration with one of my former colleagues, Com. Dmitriev. The results were interesting but at first no one seemed to be willing to further study the question, and at any rate it was clear that only a beginning had been made and the method used was rather cumbersome.

At this stage the application of the X-ray method seemed to suggest itself as an obvious solution of the problem, and it was with great pleasure that about 1930 I became acquainted with the beginnings of the work of Dr. Mehl and his collaborators. It did not take me long to see that the problem was conceived in a broad and truly scientific manner and that there was every reason to expect that the final solution of many of the problems coupled with the Widmanstätten structure was at hand. One of the most promising postulates of these new studies was that the lattice of the precipitate forms directly with a minimum shift of atoms from a crystallographically "close" plane in the parent lattice. In the present paper this view is amply vindicated.

With reference to the crystallography of cementite and the Hendricks "octahedron," reproduced in Fig. 10, I would mention that Westgren advances the view<sup>41</sup> that his "coordination polyhedron" better agrees with the supposed location of the carbon's atoms than Hendricks'; thus, it seems that here again is an interesting side problem to be tested.

The 6 to 9 cementite pictures are very interesting; I quite agree with the author that the volume changes at the  $A_1$  transformation are the cause. At one of the recent exhibitions of the Royal Photographic Society in London I showed some high-magnification photographs of distorted cementite crystals in slowly cooled steel, and I think that these and like pictures can prove the existence of considerable tensions in certain areas of hypereutectoid steels; as a result of such tensions the cementite plates in my specimens were bent and distorted more or less like mica plates.

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<sup>41</sup> A. Westgren: Cementitens Kristallstruktur. *Jernkontorets Ann.* (1932) 457.

With reference to the occurrence of Widmanstatten figures in pure iron, the photograph by Osmond in his book *On Crystallography of Iron* seems to be a sufficient proof of that particular phenomenon, and these pictures also appeared in Sauvour's *Metallographist*.

Finally, must be mentioned the paragraph on corrosion figures. It is to be hoped that the author will find time in the not too distant future to apply his method to the final settlement of the problem of the possible relation between the axial planes of neighboring grains and between the axial planes of the surrounding grain and the central one. This problem always seemed to me to be a fascinating one, and now I feel that the author has shown by his papers that we can expect from him the solution, besides many others, of that particular problem also.

R. H. ABORN and E. C. BAIN, Kearny, N. J. (written discussion) — We are particularly impressed with the authors' careful inspection of the loci of carbide plates as separated out of austenite crystal grains. It is a credit to their painstaking technique that they have been able to demonstrate that carbide rejection occurs upon crystallographic planes other than the (111), long recognized as the probable location of ferrite, the mode of separation of which has also been adequately cleared up by them. Since its inauguration, we have followed the work of Dr. Mehl and his associates on orientations of precipitated phases with the keenest interest and with admiration, particularly in view of their sound viewpoint and fundamental analysis of the problem.

In this latest paper the authors have again broadened the scope of the term Widmanstatten by including martensite. Clearly martensite logically belongs in the same category with many other structures classed by these authors as Widmanstatten figures. One cannot but wish that the language afforded a generic term for these structures, so that the word Widmanstatten might have preserved its original significance. However, we have no suggestions to offer and the authors have undoubtedly given this point considerable thought.

Concerning the facts of martensite formation there can be little disagreement. The recent microcinema work of Dr. Hanemann and his associates Hofmann and Wiester<sup>42</sup> justifies fully the concept of the authors of this paper. In their interesting moving pictures the instantaneous formation of the so-called "needles" of martensite in austenite grains, recorded as traces of planes not too far removed from the (111), on the surface of polish seems quite conclusive.

Mehl and his associates quite properly point out that the "upsetting" hypothesis of one of the present writers<sup>43</sup> is inadequate by virtue of its failure to predict the orientations that have been found by Sachs and his coworkers. We would suggest that the upsetting theory is perhaps not so much incorrect as incomplete, since the Sachs concept of transformation may, for each unit crystal cell, or small block of cells, still be resolved into an upsetting action for each of the several orientations.

This calls to mind another point upon which it would be interesting and instructive to have the authors' comments. How far may we safely accept the work of Sachs and his coworkers as representing the mechanism of martensite formation in the typical polycrystalline austenite of commercial steels? Since the formation of martensite certainly occurs in a stepwise manner one is compelled, regardless of his opinions of the atomic rearrangement, to concede that the untransformed austenite flows plastically to a significant extent in the early stages of the transformation, rapid though the transformation may be. This circumstance demands new orientations in the unchanged austenite and hence a variety of orientations in the martensite over limited ranges.

<sup>42</sup> H. Hanemann, U. Hofmann, u. H. J. Wiester: Die Gefügeänderungen des Stahles beim Harten und Anlassen. *Archiv f. Eisenhüttenwesen* (1932-1933) 5, 199.

<sup>43</sup> E. C. Bain: Nature of Martensite. *Trans. A. I. M. E.* (1924) 70, 25.

This situation was the one found by Heindlhofer and Bain;<sup>44</sup> indeed, these general distortions seem to have obscured the systematic assortment of orientations found by Sachs. If there are no ruptures in the product of the transformation of a grain of austenite, there must be a fairly wide general or random variation in orientation as well as in spacing (elastic deformation). On this basis one might suspect that the martensite from large, un-reinforced, single crystals of austenite, as employed by Sachs, would carry cracks which would in turn force a new interpretation of his results. This seems worthy of consideration because in X-ray diffraction with "white radiation" ordinary martensite produces radial streaks rather than the distinct spots recorded by Sachs.

G. KURDJUMOW, DNJEPROPETROWSK, Russia (written discussion\*).—This work by Mehl, Barrett and Smith, as well as the earlier work by Mehl and his collaborators on the Widmanstätten structure, is of great importance for an understanding of the mechanism of phase changes in the solid state. These several works have given us a large amount of experimental data concerning the orientation relationships shown by precipitated phases. From these studies we now know that an orientation relationship can exist between a precipitate and the matrix phase even when the lattice of the precipitate is complicated in structure ( $\text{CuAl}_2$ ,  $\text{Fe}_3\text{C}$ ). These authors have shown that in such orientation relationships planes and directions that have similar structure in the two lattices concerned (the original and the new lattice) play an important role. From this fact definite conclusions concerning the mechanism of formation of the first nuclei of the precipitate can be made.

If a Widmanstätten structure is formed upon precipitation, two relationships may exist, between the new and the matrix phase, according to the studies of the writer:

1. A definite arrangement of the precipitated *crystallites possessing regular outward form* with respect to the matrix crystal.

2. A definite orientation of the *lattice* of the precipitate with respect to the lattice of the old (irrespective of outward form).

For an understanding of phase transformations it is important to know whether a lattice orientation relationship is present even when the crystallites have no regular arrangement. The relationship between lattice orientation and external form of precipitated crystallites has recently been studied by Straumanis and Weerts<sup>45</sup> for Cu-Zn and Ag-Zn alloys. From this work we know that the lattice orientation of the resulting phase may remain the same while the outward form of the arrangement of crystallites may vary, and many times is not pronounced. It was also shown by Straumanis and Weerts that the lattice orientation relationships remained the same with different heat treatments. In the course of the last three years orientation relationships in several examples have been investigated and lattice orientation relationships have been observed in almost all cases studied.<sup>46</sup> It may be thus concluded that lattice orientation relationships upon transformation in solid state are entirely general phenomena.

For the formation of regular external form, on the other hand, special conditions during precipitation are necessary, as Mehl and his collaborators have shown in their beautiful series of papers on Widmanstätten structures.

Transformations are known, however, which lead to the formation of crystallites with sharp boundaries and regular arrangements. This is the case with the formation of the martensitic intermediate lattice in eutectoid alloys. It can hardly be doubted

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\* Translated from the German.

<sup>44</sup> K. Heindlhofer and E. C. Bain: A Study of the Grain Structure of Martensite *Trans. Amer. Soc. Steel Treat.* (1930) **18**, 70.

<sup>45</sup> M. Straumanis and J. Weerts: *Ztsch. f. Physik* (1932) **78**, 1.

J. Weerts: *Ztsch. f. Metallkunde* (1932) **24**, 265.

<sup>46</sup> Cf. G. Sachs: *Ztsch. f. Metallkunde* (1932) **24**, 241.

that the formation of this intermediate lattice (which always forms upon drastic undercooling) consists in a mechanical rearrangement of the lattice of the original phase without concentration change.<sup>47</sup> In this case there are no growth processes in the usual sense; each individual crystal forms suddenly, in a very short period of time<sup>48</sup> and the transformation proceeds only by the formation of new crystallites. With such a mechanism the regular arrangement and sharply defined external form of the crystallite are easily understood.

The martensite-like structures that form upon the precipitation of the  $\alpha$  phase from  $\beta$  brass in quenched alloys at low annealing temperatures suggested to Straumanis and Weerts that the  $\alpha$  crystallites probably result from lattice rearrangement. This structure differs from that formed on slow cooling in the fact that the  $\alpha$  phase forms without concentration changes. It was assumed that the concentration changes had already been prepared for in the  $\beta$  crystals, as Hengstenberg and Wassermann<sup>49</sup> have shown to be true in the precipitation of CuAl<sub>3</sub>. At intermediate annealing stages the transformed regions of the new phase act as large nuclei for further growth; at higher temperatures the growth processes markedly change the external form of the crystallites. With slower cooling the mechanism consists in a formation of  $\alpha$  nuclei and the growth of these nuclei to large crystals. The precipitated crystals in this case have the form of true needles whereas those formed at low annealing temperatures are platelike.

When the formation of a new phase does not lead to sharply defined crystallites regularly oriented we may, nevertheless, assume that the same type of atomic rearrangement mechanism obtains in the formation of nuclei but in relatively small regions. The mechanism of nuclei formation has been discussed by Mehl and his coworkers for several cases upon the basis of orientation relationships. They have shown how these lattice transformations can proceed. With the explanation of the formation of Widmanstätten structures these workers have taken lattice orientation relationship as a fundamental factor; the external form of the precipitate, however, is determined by crystal growth. The formation of platelike precipitates (which is frequent), Mehl and Barrett have explained by growth in the following way. The nuclei form in regions of suitable concentration by a definite rearrangement of atoms (regular inversion in small lattice regions). The nuclei then grow quickly along the plane in which the arrangement of the atoms differs but little from the arrangement of one of the planes in the new phase. The growth of the nuclei in the direction perpendicular thereto leads to a shearing movement of lattice planes.

I should like to ask whether the formation of Widmanstätten structures upon slow cooling always proceeds by the formation of oriented nuclei and subsequent growth. Are there not cases, even on slow cooling, in which the formation of the new phase in an ordered atomic rearrangement involves rather large lattice regions, and in which further growth in the usual sense influences the external form of the resultant crystallites only slightly? Such an explanation of the Widmanstätten structure is not conceivable in the case of the slowly cooled  $\beta$  phase in the Cu-Zn system; the growth in this case plays a definite role. The nuclei are much smaller than resultant needles. In connection with formation of ferrite the explanation given does not seem to be impossible. In its favor there are the sharp boundaries of the crystallites, the necessarily carefully adjusted conditions upon cooling (to obtain the figure), and the fact that the arrangement of the platelike crystals is the same as in martensite. In this case there is, naturally, the question of concentration changes. Such changes could be under-

<sup>47</sup> G. Kurdjumow and G. Sachs: *Ztsch. f. Physik* (1932) **64**, 325.

G. Kurdjumow: *Archiv f. Eisenhüttenwesen* (1932-33) **6**, 117.

<sup>48</sup> H. Wiester: *Ztsch. f. Metallkunde* (1932) **24**, 276.

<sup>49</sup> J. Hengstenberg and G. Wassermann: *Ztsch. f. Metallkunde* (1931) **23**, 114.

stood, for instance, by a crossing of the equilibrium line  $A_{221}$  without the formation of nuclei, but with a supersaturation of the  $\gamma$  phase; regions of low carbon concentration in the  $\gamma$  crystal result from diffusion within the  $\gamma$  phase, and these regions can at this time transform into the  $\alpha$  phase, the final concentration being attained by diffusion.

If, with the formation of new phases with an ordered arrangement of crystallites, the nuclei are smaller and the crystallites are formed by growth, their arrangement and form must depend upon the growth characteristics of the new phase. When, on the other hand, the formation of the new phase proceeds nearly instantaneously by an inversion of lattice regions (that is by simple shear), it may be expected that the arrangement of crystallites (plates) should show only the symmetry of the original phase.

The production of rather large crystallites of the precipitated phase by mechanical lattice transformation of this latter type appears to be especially probable upon the annealing of undercooled solid solutions; that is, at low temperatures at which growth is very slow. The mechanism of transformation would in this case appear to differ from the mechanism of the martensite transformation. Although with the martensite transformation no diffusion obtains previous to the lattice change, and occurs only as a subsequent phenomenon upon the decomposition of the resulting intermediate tetragonal lattice, in this case, according to Hengstenberg and Wassermann, diffusion may precede the lattice change.

I have already stated that the results of the last few years of study suggest that a regular lattice reorientation mechanism is probably the general phenomenon of transformations in the solid state. Instances are known, however, in which the lattice of the new phase has a random orientation. An example is the irregularity of the orientation of the ferrite and cementite lattices observed by myself and Iwensen<sup>50</sup> during the formation of troostite. The formation of cementite upon annealing shows no regular orientation, judging from rotation photographs of tempered austenite single crystals. It might therefore be concluded that the nuclei possess no regular orientation, and must result from some other sort of mechanism during transformation. It is, however, more probable that the irregularity is a result of a secondary phenomenon similar to recrystallization. The presence of such secondary influences has been shown by Ageew and myself for the annealing of the  $\beta'$  phase in the Cu-Al system (nomenclature of Obinata). Crystallites of the  $\beta'$  phase were found to be oriented with respect to the original  $\beta$  single crystal. After decomposition to  $\alpha + \gamma$  the rotation photograph showed no regularity to the interference spots. This lack in orientation relationships existed only in the surface layer, however. After polishing and etching a regular orientation of the lattice of the  $\alpha$  and  $\gamma$  crystallites was found. It is possible that disturbances at the surface had led to recrystallization.

R. F. MEHL, (written discussion).—Although Professor Sauveur's remarks require no reply they afford me an opportunity to say that the work he performed with Dr. Chou on Widmanstätten figures in pure iron, and the discussion I had with Professor Sauveur in his study several years ago on Dr. Chou's work, led to my interest in the general subject. I am happy to acknowledge this indebtedness.

In a somewhat similar way Colonel Belaiew is also partly responsible for my own efforts, for he has interested himself in Widmanstätten figures for many years and has made the great bulk of the contributions to the subject. Westgren's modification of Hendricks' solution of the  $\text{Fe}_3\text{C}$  structure was unknown to us when this paper was written. Westgren, however, changed the positions of the carbon atoms in the  $\text{Fe}_3\text{C}$  lattice with only a very slight shift in the positions of the iron atoms. Since our argument apparently must be built on iron atoms alone, the new structure for  $\text{Fe}_3\text{C}$  does

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<sup>50</sup> Second reference of footnote 47.

not alter the argument given in the paper. It is possible, however, that the assumption of the unimportance of the carbon atoms may be wrong, and that Westgren's new structure may lead to a more complete solution than that given here. Thus far we have not been able to produce this, for the problem is complicated and our data on the orientation of the  $\text{Fe}_3\text{C}$  plates are not very precise.

Messrs. Aborn and Bain are justified in demurring at the general term Widmanstätten figure, used in this series of papers. When the work started there seemed many reasons for the choice of the term, as may be inferred from Colonel Belaiew's brief history of the subject. But as the work proceeded and as data came from other sources, its fitness became less certain. Thus martensite, though identical with the meteoric figure in crystallographic structure differs from it in microstructure, even though showing some similarities. Furthermore, we have observed microstructures resulting from the decomposition of some solid solutions which show extremely little resemblance to the meteoric structure. At present a better term would be "transformation and precipitation structures," though I now hesitate to change the term.

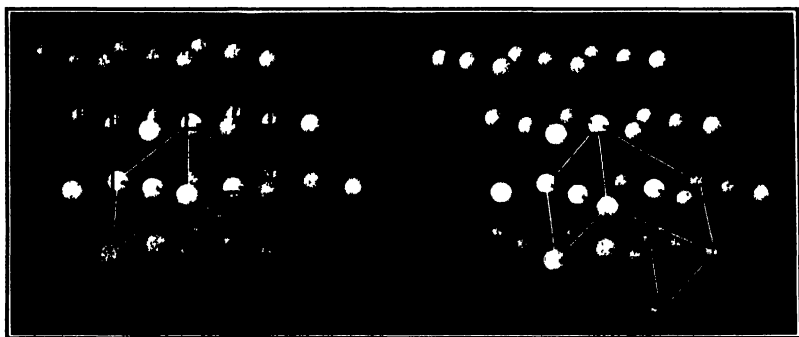


FIG. 20.

FIG. 21.

FIG. 20.—THE AUSTENITE LATTICE, REPRESENTED AS IN FIG. 1*b*, LEFT

FIG. 21.—THE FERRITE LATTICE, REPRESENTED AS IN FIG. 1*b*, CENTER AND RIGHT

The ingenious explanation offered by Mr. Bain some years ago for the formation of the tetragonal lattice in martensite doubtless led to much of the present work on transitional phases and, I suspect, encouraged Kurdjumow and Sachs' efforts on the same problem. There can be no doubt that the "crystal upsetting" process may be considered as a partial solution to the problem—we have not used it, since our primary interest was the orientation relationships existing between the austenite and ferrite (both cubic and tetragonal) lattices. A simple "crystal upsetting" process would place the tetragonal axis of the tetragonal lattice parallel to the cubic axis of the austenite, which is not the case; the complete crystallographic specification for the change can be written as follows:

$$\begin{aligned}(110)\gamma &\parallel (100)\alpha \\ [001]\gamma &\parallel [001]\alpha\end{aligned}$$

This specification would lead to three and only three orientations, none of which corresponds to the observed orientations. Nevertheless, a unit cube of austenite may be considered as passing through the "crystal upsetting" process. This is shown in Figs. 20 and 21, prepared from models made by Dr. D. W. Smith in this laboratory.

In Fig. 20 the unit face-centered cubic lattice is represented by the balls connected by white sticks. The unit body-centered tetragonal lattice pointed out by Mr. Bain is represented by the white balls. In Fig. 21 the same groupings are shown after the

transformation. Here we may see that the unit body-centered tetragonal lattice has become the body-centered tetragonal lattice of axial ratio approximately 1.07, or for the complete transformation, the body-centered cubic lattice. It is obvious that the face-centered cubic unit cell in austenite has been "upset." This can be shown, however, only with a proper selection of the unit face-centered cubic cell in Fig. 20; a selection of one of the other possible unit cell configurations does not lead to this result.

There can be no doubt, as Messrs. Aborn and Bain point out, that in polycrystalline materials a number of effects are present that rob the ideal orientation relationships of precision. The wide scatter in the directions taken by martensite "needles," shown in Fig. 19, is proof of this. No doubt deformation in the original austenite during the initial formation of a complex of orientations leads to new orientations on additional transformation deviating from the ideal positions; impedance to flow at grain boundaries is doubtless an additional important source of disturbance. The absence of the latter effect in the single crystal used by Kurdjumow and Sachs probably favored the rather sharply defined positions they observed. The solution proposed by Kurdjumow and Sachs is the general solution—in polycrystalline samples of small grain size no doubt but a few of the 24 possible orientations may obtain, perhaps sometimes only one. This is the familiar degeneracy noted previously in this series of papers.

Dr. Kurdjumow very properly points out that the study of Widmanstätten figures involves a study of the relation of the outward form of the segregate particles to the orientation of the matrix solid solution, and also a study of the orientation relationships of the lattices of the two lattices concerned. This distinction has been made throughout this series of papers. The orientation relationships are susceptible to a rather direct attack, but the conditions leading to the development of outward form are not well known. It seems certain that the outward form is not wholly determined by the mechanism of lattice change, but that growth factors determined by the nature of the parent solid solution are important. Thus  $\alpha$  brass formed from  $\beta$  brass on slow cooling rates is acicular in form, but platelike when formed at low temperatures; this change is one from a body-centered cubic lattice to a face-centered lattice. In the reverse type of transformation, from face-centered cubic to body-centered, there is no evidence of true needle formation, yet the mechanism of lattice change is the same; apparently the outward form is determined by growth factors in turn determined by the lattice of the parent solid solution. The recent work by D. W. Smith<sup>51</sup> and that by Dr. O. T. Marzke,<sup>52</sup> have helped to clarify the matter, though we still lack general principles.

I can hardly believe that the diffusion of carbon in undercooled austenite can be so fast that large areas of austenite may transform as units similar to the transformation of martensite from austenite. I know of no facts that cannot be explained by the formation of small nuclei and subsequent growth, as originally postulated.

The type of orientation relationship found in Widmanstätten figures is, I suspect, much more prevalent than has been supposed. Certainly some recrystallized metals show a preferred orientation related to the preferred orientation subsisting in the cold-worked metal before recrystallization; I suspect that this is a general tendency in the recrystallization process, often not found because of inadequate analysis, or because the annealing has been at such temperatures that the natural movement of the grains has largely eliminated it. The now well-known phenomenon of the formation of overgrowths, as when one salt crystallizes upon another, shows many analogies

<sup>51</sup> D. W. Smith: A Study of Segregate Structures in Copper-tin and Silver-zinc Alloys. *Trans. A. I. M. E.* (1933) **104**, 48.

<sup>52</sup> O. T. Marzke: Precipitation of Alpha from Beta Brass. *A. I. M. E. Contribution* 29 (1933). Abstract and discussion in *Trans. A. I. M. E.* (1933) **104**, 64.



to that of the formation of Widmanstätten figures; the crystalline interface is bounded by lattice planes in the two lattices which show similarity in pattern and in interatomic distances. I believe that many eutectic structures will also be found to show this sort of relationship.

Very closely parallel to this case is that of films—oxide, sulfide, iodide, etc.—on metals. It has long seemed likely to me that such films, upon proper analysis, will often be found to show a similar sort of orientation relationship. Such an orientation relationship would be important in determining the properties of the so-called protective or passive films on metals, leading, when the film is coherent and tightly bound, to remarkable protection against corrosion. It is more than a little likely that one condition for the formation of a protective film is the existence of such a relationship, for such a relationship would demand a tight atomic bonding of film to metal, recalling the stability of gases adsorbed in a similar way on the surface of metallic catalysts and the stability and strength of oil films on water, which show a preferred arrangement of molecules.

Dr. Kurdjumow's reference to the orientation of ferrite and cementite during the formation of troostite is timely. Recent results in this laboratory on the orientation of ferrite in pearlite have proved that the ferrite does not have random orientation but that it has a relatively small number of orientations throughout a large pearlite grain, as ferrite has in martensite; it now seems certain that the orientation of ferrite in pearlite is likewise determined by the orientation of the original austenite lattice, that pearlite is therefore a sort of Widmanstätten figure. I suspect that ferrite and cementite in troostite, which usually is lamellar ferrite and cementite of extremely fine texture, would likewise be found to show this relationship upon proper analysis.

# An X-ray Study of Iron-silicon Alloys Containing 0 to 15 Per Cent Silicon

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(New York Meeting, February, 1933)

THE literature on the binary alloys of iron and silicon has been reviewed by Stoughton and Greiner.<sup>1</sup> Another even more extensive and detailed survey of the present knowledge has been prepared under the auspices of the Alloys of Iron Research Committee by Greiner, Marsh and Stoughton. Since the latter survey has already been issued in its preliminary form, it will be unnecessary to review the literature in the present article. However, in this connection there should be noted the important work on the crystal structures of the iron-silicon alloys by Phragmén,<sup>2</sup> who investigated the entire system, identified the various phases and determined the homogeneity ranges of these phases.

It was evident in the surveys cited above that in the range from 0 to 15 per cent silicon, which includes the commercially most important alloys, the results obtained by thermal analysis, microscopic examination and the determination of electrical, magnetic and mechanical properties were extremely confusing. From time to time various compounds between iron and silicon have been postulated to account for the results yielded by the classical methods, and much argument has ensued. It was presumed that if compounds occurred which are sufficiently diverse in their properties to account for the characteristics of the alloys, they should be recognizable as separate phases but satisfactory proof of this sort has not been found by thermal or microscopic methods. Contributing to the confusion is the fact that the electrical, the magnetic and some of the mechanical properties are "structure sensitive"; i. e., they are influenced to a marked degree by the presence of minute amounts of impurities, the specific characters of these impurities, the grain size, the character of the grain boundaries, small general or local strains, etc. Thus interpretations of the discontinuities in the various property versus composition curves that identified these discontinuities with phase changes or compound formation have always been open to question.

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<sup>1</sup> B. Stoughton and E. S. Greiner: *Trans. A.I.M.E.* (1930) **90**, Iron and Steel Div., 155

<sup>2</sup> G. Phragmén: *Jnl. Iron and Steel Inst.* (1927) **116**, 397. See also his discussion of the article by Stoughton and Greiner.

The X-ray crystal-structure analysis might be expected to give useful information on such matters. It indicates definitely the existence of phases in a way that generally leaves no doubt, and the quantities measured, namely, the dimensions of the unit lattices, are not "structure sensitive" in the sense stated above. The effect of minute amounts of impurities, which enter into the lattice and thus change the lattice dimensions, is generally beyond the accuracy attainable at present in crystal-structure work. The question, of course, remains whether the phase transformations are likewise "structure sensitive." The well-known effect of removing the last traces of water upon the boiling and freezing points of certain substances is evidence in this connection. It seems clear, however, that the abnormally large effects on phase transformations produced by traces of impurities give way to "normal" effects at impurity concentrations greater than certain limiting, but rarely known, minute amounts. In alloy systems it is safe to say that the great majority of the practical and theoretical problems involving phase transformations are concerned only with the "normal" behavior. Therefore, in dealing with such materials and in all cases assuming that equilibrium has been attained, we may reasonably proceed on the basis that phase transformations are not "structure sensitive." The alternative basis, while interesting, would be not only highly academic but apt to be entirely futile as far as results of practical interest are concerned. The X-ray structure analysis should therefore give a true picture of the natures and the ranges of existence of the phases in the iron-silicon alloys when these phases can be retained by quenching to room temperature.

The present article gives the results obtained in the first part of a research program devoted to X-ray studies of ternary alloys in which iron is the main and silicon a minor component. The results given below on the binary alloys of iron and silicon form part of the base line for these studies. While Phragmén's original work included compositions between 0 and 15 per cent silicon, he used only four alloys in this range, the lowest of them containing 3.5 per cent silicon; a fifth composition was added in his discussion of Stoughton and Greiner's article. While Phragmén's experimental results were confirmed in the present investigation, they were found to be insufficient; the range below 5 per cent silicon proved to be especially important.

The particular object of the present investigation was the detailed study of the range of composition up to approximately 15 per cent silicon. The more or less generally accepted idea is that over this range of composition there is a series of solid solutions of silicon in  $\alpha$  Fe, except, of course, for the region covered by the " $\gamma$ -loop." The results below indicate that we must either modify this conception or else accept the idea that important changes in properties may arise merely from distributing the solute atoms among certain definite positions in the lattice. A

final, conclusive interpretation cannot be given on the basis of present results, for the reason that the precision attained in this investigation, although fairly high, was not high enough. The report is made at the present time because (1) the results indicate that the behavior of alloys in this range is more complicated than usually is supposed; (2) there is some doubt whether the necessary precision can be attained and (3) the development of the apparatus and technique required is likely to be a long process. Partly because of this situation and partly because of the extreme confusion among the data obtained by other methods, the present writers will make no attempt to "reconcile" their data with any of the phase diagrams previously proposed, nor will they suggest a new diagram on the basis of the new data.

### MATERIALS

The silicon was specially purified material made by the Electro Metallurgical Corporation. The analysis of this material shows: Si, 99.79 per cent; Fe, 0.027 per cent; Al, 0.008 per cent; Ca, 0.014 per cent; C, 0.004 per cent; O<sub>2</sub>, 0.002 per cent; N<sub>2</sub>, 0.10 per cent; and H<sub>2</sub>, a trace.

TABLE 1.—*Impurities in Iron and Alloys*

Element	Electrolytic Iron	Alloys					Method
		30	24	25	27	32	
C	0 01	0 01					Spectro
Cu	0 01	0 01					Spectro
Al	0 000	0 003					Spectro
Ca		<0 01					Spectro
Si	0 001						Spectro
Mn	0 01	0 01					Spectro
Sn	0 005	0 002					Spectro
S			0 010		0 005		Evolution
P				0 031		0 028	Phospho- molybdate

Electrolytic iron prepared many years ago by Burgess from sulfate solutions was available. This material in lump form was heated in a stream of purified H<sub>2</sub> at temperatures from 950° to 1050° C. for 48 to 72 hr. to reduce the sulfur and oxygen contents. A spectroscopic analysis of the iron is given in Table 1.

Owing to the small size of the alloy ingots, complete analyses for the impurities could not be made on any one alloy. All the analytical determinations of impurity except those in the silicon are given in Table 1.

The electrolytic iron used for the spectroscopic analysis had been melted in vacuo under the same conditions as the silicon alloys (see below).

## X-RAY METHODS

Bohlin focusing cameras as designed by Phragmén<sup>4</sup> were used for determining the lattice constants. These cameras have been very carefully calibrated against pure NaCl, using the radiation from both copper and iron targets. The lattice constant for NaCl upon which the calibrations are based was taken as 5.6280 Å. Film shrinkage is allowed for by measuring the total length of the darkened area on the film that extends between two knife edges built into the camera; all measurements are corrected back to the same length as the original calibration film. Film measurements can generally be checked to  $\pm 0.1$  mm. Radiation from an iron target was used throughout the investigation.

For determining the lattice constants, only the three most deviated reflections were used; namely, the reflections of  $K\alpha_1$  and  $K\alpha_2$  radiations from the 220 plane and that of  $K\beta$  from the 310 plane. For these reflections a shift of  $\pm 0.2$  mm. in the positions of the lines corresponds to a change of  $\pm 0.001$  Å in the lattice constant. For no film reported in Table 2 did the maximum difference between the values of the lattice constant  $a$  calculated independently for each of the three lines exceed 0.001 Å. Most of the films were measured twice, and in many cases the same film was measured by two observers. The maximum difference between independent determinations of  $a$  from any film, whether made by one or both observers, was 0.0003 Å, so that the average values are well within the experimental error of measuring the films. The error in determining  $a$  may therefore be set safely at  $\pm 0.0005$  Å.

The maximum difference between points read from the straight lines plotted in Fig. 1 and experimentally determined points, not including Phragmén's, is 0.0007 Å. The average deviation over section  $AB$  is  $\pm 0.0003$  Å; over  $CD = 0.0005$  Å. These average deviations include Phragmén's data.

The writers, therefore, feel entirely justified in stating that no point represented in Fig. 1 lies beyond the limits set by the experimental errors in determining  $a$ , and in the chemical analysis.

Throughout the article, all the measurements will be given in terms of the small-body-centered cube of  $\alpha$  Fe.

## RESULTS

The experimental results are summarized in Table 2 and Fig. 1. Phragmén's data are also included. In the diagram, the lattice constants are plotted as a function of atomic per cent silicon; this is the best form for indicating any regularities that might occur. The results were studied in

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<sup>4</sup> A description is given by Westgren: *Trans. A.I.M.E.* (1931) **93**, Inst. of Metals Div., 13.

the form of a large-scale plot in which 20 mm. = 1 atom per cent and 40 mm. =  $0.01\text{\AA}$ .

The first fact disclosed by this plot was that no single smooth curve that would represent the results within the limits of experimental error could be drawn through the whole range of points. The second fact disclosed was that two straight lines could be drawn, each of which represented one range of data faithfully. The slopes of these two straight lines are described by the following data:

Line  $AB$ , from 0 atomic per cent Si and  $a = 2.8607\text{\AA}$  to 9.00 atomic per cent and  $a = 2.8573\text{\AA}$ .

Line  $CD$ , from 9.00 atomic per cent Si and  $a = 2.8572\text{\AA}$  to 25.00 atomic per cent and  $a = 2.8213\text{\AA}$ .

While these two lines intersect at a point where  $a = 2.8573$  and the silicon content is 8.95 atomic per cent, there is a short range between 5.5 and 7.5 atomic per cent where a horizontal line might conceivably be drawn. It is indicated in Fig. 1 by the dotted line  $EF$ . It is to be noted that the existence of this range is by no means conclusively proved by the data presented; in fact, it requires considerable imagination to find it at all. The reason for indicating this rather dubious possibility will be made clear in a subsequent section. It is important to note that the slope of the line  $CD$  is approximately 3.15 times that of  $AB$ .

If we assume simple substitution and the constancy of the atomic radii and use  $r_{\text{Si}} = 1.172\text{\AA}$ <sup>5</sup> and  $r_{\text{Fe}} = 1.239\text{\AA}$ , the slope of the lines  $AB$  and  $CD$  should be  $0.00155\text{\AA}$  per atomic per cent. The actual slope of  $AB$  is  $0.00065\text{\AA}$  per atomic per cent while that of  $CD$  is  $0.00209$ . Thus the actual slopes of  $AB$  and  $CD$  are, respectively, 0.42 and 1.35 times the theoretical value. It is a curious fact, however, that the assumption of constant radii leads to a value of  $a = 2.8227\text{\AA}$  for  $\text{Fe}_3\text{Si}$  while the value found by interpolating the curve is  $2.8213\text{\AA}$ . Further consideration indicated that this close agreement is merely fortuitous.

It may also be remarked that no effect on the lattice constant greater than the experimental error resulted from changing the annealing temperature from  $724^\circ$  to  $883^\circ$  for any of these alloys. Phragmén's alloys were furnace-cooled from  $1100^\circ\text{C}$ . These facts indicate that the lattice constants are practically independent of the heat treatment provided the alloys are chemically homogeneous.

## DISCUSSION OF RESULTS

The results of the investigation have been stated in the preceding section and the writers wish to emphasize that it is necessary to keep the experimental facts clearly separated from the interpretation that may be

<sup>5</sup> This value is based on the lattice constant of the silicon used in this investigation, which has been determined recently in this laboratory by Emory Gebert. The value is  $a = 5.415\text{\AA}$ .

placed upon them. In what follows we shall set up working hypotheses and attempt to account for the experimental results on the basis of each one. It may be stated at the outset, however, that while hypothesis A has a more conventional basis than B, the two are not entirely independent.

### *Hypothesis A*

The conventional interpretation of the data as presented in Fig. 1 is to consider that each of the two linear portions of the diagram represents a single phase. The first phase would be  $\alpha$  iron in which silicon had dissolved. The second would need to be a compound that is able to

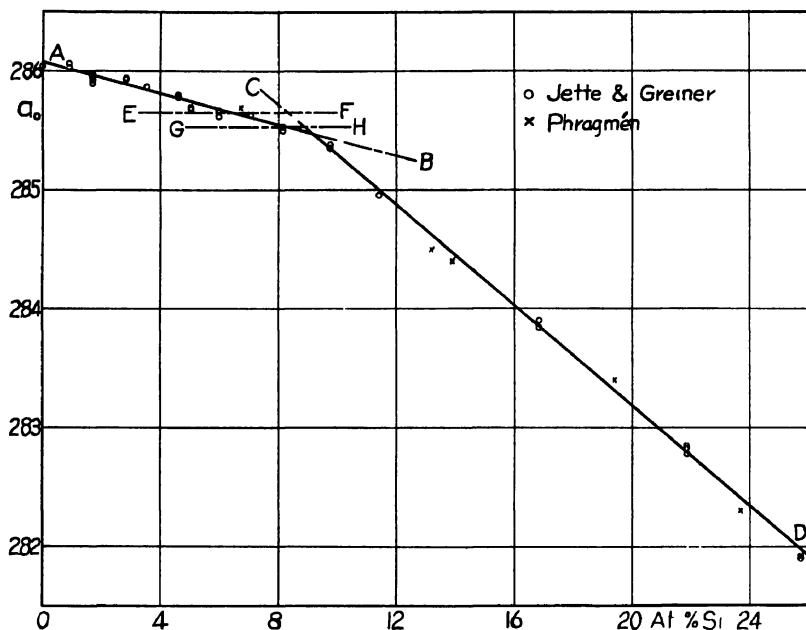


FIG. 1.—RELATION BETWEEN LATTICE CONSTANT AND COMPOSITION

dissolve either excess silicon or excess iron; in this case the only compound that can reasonably be chosen is  $\text{Fe}_3\text{Si}$ . This, of course, demands that there be an intermediate range where the two phases coexist. In the X-ray photograms such a situation is indicated by the presence of two sets of lines on the photograms, one set for each phase. For a series of alloys of different compositions but all of which have been quenched from the same temperature, the positions of the lines in each set are constant in the two-phase area. It is highly improbable, even in the present case where there is a close relationship between the two lattices, that the corresponding lines should fall in exactly the same positions. This will demand, therefore, a second horizontal line, which is indicated in Fig. 1 by  $GH$ . In spite of the facts that the present data give extremely

little, if any, support for the existence of the two-phase area, and even less support for the particular locations assigned to the lines  $EF$  and  $GH$ , this interpretation still remains a definite possibility. There are excellent reasons why it would be difficult, and perhaps even impossible, to determine the simultaneous occurrence of two phases in this particular case.

The first difficulty with this hypothesis arises from the nature of the evidence upon which the existence of the compound  $\text{Fe}_3\text{Si}$  is postulated. Over the entire range from 0 to 25 atomic per cent Si, lines corresponding to  $\alpha$  iron—*i. e.*, the lines of a body-centered cubic lattice—are found on the X-ray photograms. Beyond 12.5 atomic per cent, new lines appear which, when combined with the others, yield a face-centered cubic lattice with a cube edge twice that calculated from the  $\alpha$  Fe lines alone. These new lines are due to the fact that the silicon atoms are no longer distributed at random in the  $\alpha$  Fe lattice but have taken up definite positions. Such a phenomenon occurs rather frequently in properly annealed alloys. The large lattice, which in this case includes in its volume eight of the smaller, is called a “super-lattice,” “super-structure” or sometimes an “overstructure.” In cubic structures the superstructure lines usually occur at compositions where the ratio of solute atoms to solvent atoms is equal to or slightly in excess of one or more of the ratios 1:7, 1:3, 1:1. Phragmén found these lines at 13.2 atomic per cent, and above but not below; the present results confirm this observation. Phragmén found further that the most regular distribution of silicon atoms that would satisfy the face-centered cubic symmetry would correspond to the formula  $\text{Fe}_3\text{Si}$ . Since he also determined that the limit of this phase occurred at approximately 26.5 atomic per cent, he considered that  $\text{Fe}_3\text{Si}$  was only a distinguished point in the  $\alpha$  solid solutions and was not a true compound. For the purpose of discussing hypothesis A, we shall however, consider that it is a compound and that it forms the structural basis of a solid solution.

As far as the present writers are aware, superstructure lines have never been observed in cubic structures when the ratio of solute atoms to solvent atoms was less than 1:7; *i. e.*, below 12.5 atomic per cent of the solute. The straight line  $CD$ , however, begins at about 9 atomic per cent. It is evident that if we are to retain the present basis of argument that  $\text{Fe}_3\text{Si}$  is a distinct phase, some “explanation” must be found that will account for the constancy of slope all the way down to 9 atomic per cent, but for which the presence of superstructure lines is not crucial.

The intensities of the individual lines on an X-ray photogram depend upon the “atomic scattering factors” of the atoms concerned, and these are roughly proportional to the respective atomic numbers. From the atomic scattering factors and the arrangement of the atoms in the unit cell, “structure factors” may be calculated for all of the possible planes within the crystals. From these in turn the relative intensities of the lines may be computed. As a result of such calculations, it is found that



reflections from certain planes will be observed only if these planes contain more than one atomic species and the intensity of the lines will be a function of the difference between the atomic scattering factors of the atomic species involved. Thus, if we consider a superlattice with a cube edge twice that of  $\alpha$  Fe but containing only iron atoms, we will not find reflections from planes whose indices are 111, 311, 331, 200, 222, 420 and a number of others. If, however, the lattice contains a sufficient number of silicon atoms, and if these atoms are not distributed at random but occupy certain definite positions, reflections from these planes will occur. The lowest silicon content at which these reflections are found is apparently 12.5 atomic per cent. Reflections from planes such as 220, 400, 422, and others, for which  $(h + k + l)/2$  is an even number, will always occur regardless of the presence or absence of silicon atoms.

Let us now regard  $\text{Fe}_3\text{Si}$  as a compound that forms the structural basis of a series of solid solutions, and consider the effect of substituting iron atoms for the silicon. According to Vegard's rule, we should expect a linear relation between the lattice constant and the composition in atomic per cent such as Fig. 1 shows. This linear relationship should continue to the homogeneity limit of the phase; *i. e.*, to about 9 atomic per cent silicon. However, below 12.5 atomic per cent silicon there are not enough silicon atoms located in the special lattice planes to give the reflections that distinguish  $\text{Fe}_3\text{Si}$  from  $\alpha$  iron. Thus if we wish to maintain that  $\text{Fe}_3\text{Si}$  is the basic lattice for this entire range of composition, we must be willing to believe that, in this special case, a lattice may exist in a composition range where the only reflections that distinguish it from its neighboring phase have disappeared. To the present writers this would not seem to be impossible or unreasonable in view of the close relationship between the lattices of  $\alpha$  Fe and  $\text{Fe}_3\text{Si}$ . We would, in such an interpretation, be assuming that the interatomic forces, which lead finally to the symmetrical  $\text{Fe}_3\text{Si}$  structure at 25 atomic per cent silicon, operate in the same way at lower silicon contents even when the distinguishing superstructure lines are not present. The superstructure lines would be regarded in this argument as merely incidental. The problem of explaining the abrupt change of slope would remain whether these lines were found or not. It is to be emphasized, however, that the argument rests entirely upon the constant slope of the curve *CD* and the wide difference between this slope and that over the range *AB*.

This hypothesis would make the true solubility of silicon in iron from about 5 to 7 atomic per cent, or 2.5 to 3.5 weight per cent. This would be in accord with the general knowledge of the solubility of silicon in metals. The solubility seems always to be low; in a number of cases where the thermal diagram indicates a considerable solubility X-ray analysis has shown conclusively that the solubility is very low.<sup>6</sup>

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<sup>6</sup> Nine systems recently investigated in this laboratory have given silicon solubilities of at most a few tenths of a per cent.

Hypothesis A could be established conclusively if it were possible to demonstrate the existence of two phases somewhere in the range between 5 and 9 atomic per cent silicon, and, naturally, attempts were made to do so. If the range of the two-phase area is small, the diffraction lines corresponding to the different phases would practically coincide; *i. e.*, the two horizontals *EF* and *GH* would be very close together. The present results indicate that the difference between the lengths of the cube edges would certainly not be much over  $0.001\text{\AA}$  and, perhaps, would be well under this value. The discussion of the accuracy of the measurements given above shows that a difference of  $0.001\text{\AA}$  would correspond to a shift of 0.2 mm. in the lines. This is of the same order of magnitude as the line widths; the lines would therefore overlap and the final effect would consist largely in a broadening of the lines. Attempts were made to prove the existence of two sets of lines by measuring the intensity distribution within the lines by means of a microphotometer. While some of the lines showed a slight broadening, none of these measurements were conclusive. It will be possible to prove the existence of two phases only when cameras of much greater resolving power can be built and the accuracy of determining the lattice constants becomes at least 10 times as great as at present.

### Hypothesis B

This hypothesis is that the entire range is a single-phase solid solution with properties that vary continuously, although not uniformly, as the composition changes from pure iron to 15 weight per cent silicon. The straight lines *AB* and *CD* will be considered to be connected by a short curved section between approximately 7.0 and 9.0 atomic per cent. The failure to observe a significant effect of annealing temperature on the lattice constant of any of the alloys might be considered as evidence in favor of this hypothesis.

Phragmén<sup>7</sup> has given a diagram of the  $\text{Fe}_3\text{Si}$  structure. It will be somewhat more convenient for the discussion to shift the origin

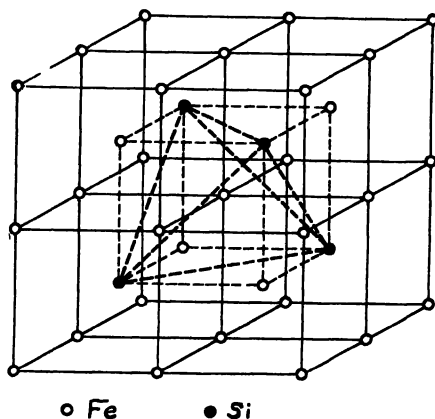


FIG. 2.— $\text{Fe}_3\text{Si}$  LATTICE.

in this diagram along the cube diagonal until we obtain the result given in Fig. 2; this is the form used by Bradley and Jay<sup>8</sup> in their discussion of the

<sup>7</sup> Discussion of article Stoughton and Greiner: *Trans. A.I.M.E.* (1930) **90**, Iron and Steel Div., 187.

<sup>8</sup> A. J. Bradley and A. H. Jay: *Jnl. Iron and Steel Inst.* (1932) **125**, 339.

analogous compound  $\text{Fe}_3\text{Al}$ . All of the outer atoms are iron. The inner portion is a body-centered cube with an iron atom at the center, four other iron atoms arranged as a tetrahedron and four silicon atoms also on a tetrahedron. The last four iron atoms and silicon atoms together form a simple cube. This structure represents complete orientation of the silicon atoms in the lattice. The problem is to "explain" the change in the lattice constant as a function of atomic composition. It may be mentioned again that over the first 9 atomic per cent silicon the decrease in the lattice constant is only 0.42 as much as it should be if the atomic radii are constant and the same as in the pure elements, while for the remainder it is 1.35 times the theoretical decrease.

Starting with pure iron, the added silicon atoms enter the lattice by the usual substitution of atom for atom.<sup>9</sup> The fact that the lattice does not decrease in size as rapidly as it should can be interpreted in either of two ways: (1) the silicon atom retains its size and does not fill up the space left by the iron atom which it replaced or (2) the silicon atom expands. In the latter case the silicon atom would have a radius of  $1.211\text{\AA}$  instead of  $1.172$ . This seems like a rather large change. Silicon has the same lattice as the diamond, and this structure is possessed only by elements whose physical properties are essentially nonmetallic; *e. g.*, carbon, gray tin, etc. Silicon's position in the periodic table, however, indicates that it may have either metallic or nonmetallic properties. That its radius should change when it is transferred from the nonmetallic diamond structure, where it is surrounded by other silicon atoms, to a strictly metallic environment, where it is surrounded by iron atoms, does not seem at all improbable. It may be remarked that an explanation of this sort is also necessary even if this range of composition is considered to be a separate phase, as under hypothesis A.

At 6.25 atomic per cent, one atom in each sixteen is silicon. This means that of all the small-body-centered  $\alpha\text{Fe}$  cubes one-eighth will contain one silicon atom each. It will be more convenient at this point to look upon our problem as one of completing the silicon tetrahedron in the 16-atom superlattice. At 6.25 atomic per cent there will be in a completely homogenized alloy one silicon atom in each superlattice. It is obvious that, up this point, it would not matter in the least which position the silicon atom occupied in the superlattice, and the X-ray analysis would be unable to detect its position unless it were located at the center of the cube (coordinates  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ ). In this event a set of superstructure lines should be found that would differ in certain details from those found at 12.5 atomic per cent. No such lines were observed.

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<sup>9</sup> This has not been checked by the experimental determinations of the density in the present investigations. Phragmén's work establishes the type of substitution and, in any case, the iron and silicon atoms are so nearly the same size that interstitial solid solution is impossible.

There is, therefore, no reason to be found in these results for postulating the compound  $\text{Fe}_{16}\text{Si}$ .

Beyond this composition, however, some cells would have two silicon atoms, and at 9.38 atomic per cent one-half of the superlattices would be so constituted. Again we assume completely homogenized alloys. We may logically suppose that in such materials the tendency towards taking up definite positions in the superlattice will be operative, and that in this case the second silicon atom will be located so that the two silicon atoms will occupy two of the corners of the silicon tetrahedron shown in Fig. 2. It is at approximately this composition that the sharp change in slope is observed (Fig. 1). Why the break should occur at this point (8.95 atomic per cent) is entirely unknown. The composition corresponds nearly to  $\text{Fe}_{10}\text{Si}$ , but there is no possibility of fitting such a compound into a structure of cubic symmetry with a unique position for the silicon atom, and of reconciling this structure with the observed diffraction lines. At 12.5 atomic per cent every superlattice would have two of these tetrahedron corners occupied by silicon atoms, and at or just beyond this point the superlattice lines appear on the X-ray photograms. Since the change in lattice constant with composition is continuous through this range, no special significance is to be attached to the formula  $\text{Fe}_7\text{Si}$ , which corresponds to 12.5 atomic per cent.

For the remainder of the range up to  $\text{Fe}_3\text{Si}$ , the process consists in completing the silicon tetrahedron. The change in slope would be "explained" by assuming that the formation of the silicon tetrahedron involved a contraction caused by the silicon atoms attempting to establish essentially the same mutual relationship as exists in pure silicon. That this is no very conclusive argument will be evident. The matter will be discussed further in the next section.

It must be remarked that according to hypothesis B the point at which the change of slope occurs should be independent of temperature, since a change of temperature should not change the orientation of the silicon atoms once this has been established.

#### *General Problem*

On the whole, the most difficult matter to understand is the change of slope. This difficulty, however, would be nearly as great if the experimental results were so inaccurate that a single smooth curve could be drawn for the entire range of 0 to 25 atomic per cent.

The relation between the slope of the parameter curve, composition and atomic radii for this system is

$$\frac{da}{dP} = \frac{4}{100\sqrt{3}} (r_{\text{Si}} - r_{\text{Fe}})$$

where  $P$  is the atomic per cent of silicon. If  $r_{\text{Fe}} = 1.2387\text{\AA}$  and  $r_{\text{Si}} = 1.1724\text{\AA}$ , the theoretical slope is 0.000153. Taking the measured slopes

of the lines  $AB$  and  $CD$  and assuming that  $r_{Fe}$  is unchanged, we obtain  $r_{Si} = 1.2106$ , for the section  $AB$ , and  $r_{Si} = 1.1483$  for the section  $CD$ . In other words, *if only the silicon atom changes*, its radius would need to increase by  $0.038\text{\AA}$  in order to fill the space available to it over the section  $AB$  and its radius would have to be decreased by  $0.024\text{\AA}$  for section  $CD$ . The suddenness of this large total change of  $0.062\text{\AA}$  is remarkable; at a maximum, the composition range where this change occurs cannot be more than 3 or 4 atomic per cent if we accept hypothesis A, or under 1.5 atomic per cent if we used hypothesis B.

It is general experience in X-ray studies that in metallic systems in which compound formation occurs, the observed lattice parameters of the compounds are appreciably less than would be calculated from the atomic radii. This experience might be used as confirmation of hypothesis A. On the other hand, the change in slope is closely associated with the second stage in building up the silicon tetrahedron. Since there then exists the opportunity for mutual influence of silicon atoms upon each other, the sharp decrease in the radius of the silicon atom could perhaps be understood and we might use these arguments as support for hypothesis B. It is evident, however, that there is no clear distinction between the two hypotheses to be found in the change of slope; the building up of the silicon tetrahedron is essential to both.

Attempts were made to find distinctive differences by annealing at low temperatures. Alloys containing 0.91, 7.07, 16.85 and 21.88 atomic per cent silicon were annealed in powder form at  $235^{\circ}\text{C}$ . for more than a month. In every case the lines on the photograms were broad and diffuse and only for the 21.88 atomic per cent alloy could measurements be made; these were none too satisfactory, but gave essentially the same results as a higher-temperature specimen. (See Table 2.) The broadness of the lines is unfortunately also subject to several different interpretations, two of which are: (1) that it is due to two phases having nearly the same dimensions and (2) that diffusion is so slow at this temperature that the silicon atoms could not completely rearrange after the severe cold work of grinding, and the alloy would not be homogeneous. Mechanical distortion of the lattice should have been removed by the long anneal. The first would fit in with hypothesis A; the second would be effective in either case.

Further progress in the solution of the problems raised in this range of the iron-silicon alloys depends upon a different character of experimental work which the writers are at present unable to perform. It has already been pointed out that hypothesis A could probably be established or rejected if an X-ray camera with at least 10 times the present accuracy were available. Since the development of high-precision cameras is a necessary part of the work in this laboratory, steps in this direction have already been taken.

Bradley and Jay<sup>10</sup> in their study of  $\text{Fe}_3\text{Al}$  have worked out methods for determining the percentage of aluminum atoms occupying the same positions as the silicon atoms with which we are concerned. Useful information undoubtedly will be found by applying these methods, although they can be used in the present case only beyond 12.5 atomic per cent silicon and therefore could not be expected to give direct information as to the nature of the phenomena occurring from 6 to 9 atomic per cent. Probably the best approach to the latter phenomena would be the study of the atomic scattering factors and, by means of these, the study of the electron distribution. The application of the Fourier analysis, as has been done by Bragg and his coworkers, would also be of assistance in this work. All of these methods require special and very accurate photometric equipment which is not available at present.

### CONCLUSION

It will be evident from the above discussion that the experimental results obtained in this investigation do not permit us to make a final decision between the two hypotheses. It is therefore impossible to draw any but tentative conclusions at the present time. The conclusions given below are based entirely upon the X-ray study; they are to a large extent independent of which of the two working hypotheses the reader may prefer. It will be obvious that these conclusions cannot be expected to apply to structure-sensitive properties over the concentration ranges where such effects develop.

1. In the range between 0 and approximately 6 atomic per cent (0 to 3.1 weight per cent) completely homogenized alloys will have properties that vary regularly in a way that would be expected of a series of homogeneous solid solutions.

2. In the range around 9 atomic per cent (4.7 weight per cent) or perhaps between 6 and 9, irregular behavior may be expected.

3. In the range above 9 atomic per cent, regular variation in the properties should again be expected up to 25 atomic per cent, but the absolute values of the quantities measured will probably indicate that the alloy is less and less "typically metallic" as the composition approaches  $\text{Fe}_3\text{Si}$ .

### ACKNOWLEDGMENTS

The writers wish to thank Prof. H. A. Webb, of the Physics Department of Columbia University, for the use of the microphotometer with which the line intensities were studied; Dr. F. M. Becket, of the Electro Metallurgical Co., for the silicon, and the Bell Telephone Laboratories, Inc. for the use of the equipment for the spectroscopic analysis.

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<sup>10</sup> A. J. Bradley and A. H. Jay: *Jnl. Iron and Steel Inst.* (1932) **125**, 339, and *Proc. Roy. Soc.* (1932) **136A**, 210.

The writers are also indebted to Mr. Frank Foote for assistance on numerous occasions throughout the work and in particular for making the photometric measurements.

## DISCUSSION

*(Robert S. Archer presiding)*

A. ST. JOHN, New York, N. Y.—Do you attribute the absence of any observable lines of a second phase in the presence of the major phase to the small quantity that might be present or to a smaller dimension of that quantity? In one instance it might be possible to apply some special methods for the detection of small quantities, whereas in the other those would not be applicable.

E. R. JETTE.—We tried to find two-phase areas by annealing at different temperatures. We also recognized that it is quite possible that if two phases do exist their parameters will be so nearly the same that there would be a great deal of difficulty in distinguishing between them. From the character of the curves, it looks as though the difference would be of the order of  $0.001\text{\AA}$ . That would mean a separation of the lines which we are using for measurement of  $0.2\text{ mm}$ . Ordinarily we cannot distinguish between two lines that are only  $0.2\text{ mm}$ . apart, except by a photometer. We have done a considerable amount of photometric work on these lines to see whether we could analyze them in any way, but could not get any conclusive results. Occasionally there seemed to be broadening of the lines, but the broadening was so slight that there was no certainty about it.

A. ST. JOHN.—I have in mind the possibility of one superlattice line occurring at a much smaller angle than anything in the normal lattice. I observed such lines in certain alloys years ago, and that the failure to observe this ordinarily is due to the small quantity present. It might be possible to apply some special focusing methods in that region which would be effective, whereas if the failure to observe lines is due to small particle size the lines would be so diffuse that they would probably not be observable.

E. R. JETTE.—If it is a question of too small particle size, there is nothing we can do about it. As for the possible existence of another superlattice with a line very far in, it is possible, although I do not think it is highly probable. In all this work we are using iron radiation and not molybdenum. The smallest deflection we can measure has a value of  $\sin^2 \theta = 0.075$ . With the Debye camera I think it is less than that, so it does not look to me as though that would be an explanation.

M. J. BUEGER, Cambridge, Mass.—Is straight substitution the only possibility for placing the silicon atoms? There is some theoretical objection to placing them where they have been placed, because the coordination of the silicon does not correspond with the coordination it usually displays. If the atoms were placed at  $(0\ \frac{1}{2}\ \frac{3}{4})$ , instead of  $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$  that would make a tetrahedral arrangement around the silicon atom.

E. R. JETTE.—That is a difficult question to answer offhand. I will think about it later on when I see the question written out, but there are two ways of drawing this superstructure. The difference consists of whether you put the silicon atoms on the edges or inside. These two lattices are equivalent, since each may be derived from the other by translation along the cube diagonal.

As for the coordination number, I do not know whether you can apply ordinary coordination notions to these metallic alloys. Silicon, of course, is a border-line element. It is in column four of the periodic system and can behave either as a metal or

nonmetal, so we cannot draw any very definite conclusions. If you put an atom that is ordinarily typically nonmetallic in a metallic atmosphere, it might do things you do not expect it to do normally.

E. R. JETTE (written discussion).—The assignment of locations to the iron and silicon atoms in the superlattice was made by Phragmén<sup>11</sup> on the basis of his examination of single crystals containing respectively 7 and 14 weight per cent silicon by the Laue method. While the details of this examination have never been published, to the writer's knowledge, it is highly probable that this arrangement is correct

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<sup>11</sup> Reference of footnote 2; also *Stahl und Eisen* (1925) **45**, 299.



# A Study of the Homogeneity Limits of Wüstite (FeO) By X-ray Methods

By ERIC R. JETTE\* AND FRANK FOOTE,† NEW YORK, N. Y.

(New York Meeting, February, 1933)

IN a recent article,<sup>1</sup> the authors reported the results of an X-ray investigation on the range of solid solutions that occurs in the iron-oxygen system in the vicinity of the compound FeO, which frequently is called "wüstite." The object of that investigation was primarily to study the unusual type of solid solution phenomena involved in this range. Briefly summarized the results were:

1. The NaCl type of lattice found by earlier workers was confirmed.
2. The lattice dimensions decrease rapidly with decrease in iron content.

3. No alloy that was a homogeneous single phase was ever found at compositions beyond 76.80 per cent Fe, while the theoretical iron content of FeO is 77.73 per cent Fe.

4. Measurements of the densities and lattice constants led to the conclusion that the form of substitution was complex, an FeO group being replaced by oxygen. Such a substitution, of course, is equivalent to removing an iron atom (or ion). The ideal unit cell of FeO can be considered as containing four groups of FeO and, thus, when this type of substitution takes place, there remain in the unit cell three FeO groups and an oxygen, or a total of seven atoms with a gross formula of Fe<sub>3</sub>O<sub>4</sub> instead of the original Fe<sub>4</sub>O<sub>4</sub>.

5. This was the only interpretation that would fit the experimental results and at the same time be consistent with (a) the previously determined fact that the FeO lattice is ionic (*i. e.*, consists of Fe<sup>++</sup> and O<sup>-</sup> ions) and (b) the chemical fact that as the oxygen content of the substance increases, ferrous iron becomes oxidized to ferric iron. The experimental results of this investigation are included in Fig. 1.

The purpose of the present investigation was to determine the limits of this homogeneity range by means of the X-ray structure analysis. This method has been applied frequently to the study of solid solutions by Westgren and his coworkers as well as by other investigators. The principle is simple: if the change in lattice constant with composition is

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<sup>1</sup> *Jnl. Chem. Physics* (1933) 1, 29.

known accurately within the homogeneity range and plotted as a curve, the limiting compositions of this phase may be found by determining the lattice constants of this phase when it is in equilibrium with the neighboring phase at various temperatures. After measuring the lattice constants of samples quenched from various temperatures, which are proved to contain the neighboring phase by the presence of the latter's characteristic lines in the X-ray photogram, reference to the curve gives the compositions corresponding to these lattice constants. The curve for the relation between quenching temperature and composition may then be plotted in the usual way.

Certain conditions must be fulfilled in order to apply this method successfully. In the first place, the accuracy of determining the lattice constants must be adequate for the task set. In any case, it is necessary to be certain of the third decimal place ( $0.001\text{\AA}$ ) and whenever the rate of change in the constant with composition is low or when the solid solution range is itself small, even higher accuracy must be attained. The second condition is that equilibrium between the two neighboring phases must be reached and retained until the end of the X-ray exposure. The third condition is that impurities that affect the lattice constant must be absent or at least reduced to a minimum; this is because the entire determination is based upon the size of the lattice. When these conditions are satisfied, the limiting compositions of solid solution phases may be determined with a high degree of accuracy.

#### PREVIOUS INVESTIGATIONS

The literature on iron-oxygen system has been critically reviewed by Ralston,<sup>2</sup> who included in his work articles appearing early in 1928. Since that time three important investigations have been reported, which are of interest in connection with the present work; namely, those by H. Schenck and Hengler,<sup>3</sup> Mathewson, Spire and Milligan,<sup>4</sup> and Pfeil.<sup>5</sup>

At the time of Ralston's review the only experimental investigation that had resulted in a thermal diagram for the range between the compositions of FeO and Fe<sub>3</sub>O<sub>4</sub> was that of R. Schenck and Dingmann,<sup>6</sup> although the review shows that other individual data could be used to amplify these results. However, the correlation between the results of the various investigations was anything but satisfactory.<sup>7</sup> R. Schenck

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<sup>2</sup> O. C. Ralston: U. S. Bur. Mines *Bull.* 296.

<sup>3</sup> H. Schenck and E. Hengler: *Archiv f.d. Eisenhüttenwesen* (1931) **5**, 209.

<sup>4</sup> C. H. Mathewson, E. Spire and W. E. Milligan: *Trans. Amer. Soc. Steel Treat.* (1931) **19**, 66.

<sup>5</sup> L. B. Pfeil: *Jnl. Iron and Steel Inst.* (1931) **123**, 237.

<sup>6</sup> R. Schenck and T. Dingmann: *Ztsch. anorg. Chem.* (1927) **166**, 113; (1928) **171**, 239.

<sup>7</sup> Reference of footnote 2, 91, Table 14.

and Dingmann attempted to obtain equilibrium between solid iron-oxygen phases and definite mixtures of CO and CO<sub>2</sub>. By plotting solid phase compositions against the ratio of CO to CO<sub>2</sub>, the limiting compositions of the homogeneous field called wüstite could be determined. These results are critically discussed by Ralston and also by Benedicks and Löfquist,<sup>8</sup> so that similar discussion is unnecessary here.

H. Schenck and Hengler investigated principally the liquidus and solidus curves of this region. They also determined, by microscopic methods, two points on the magnetite side of the wüstite area which agreed well with the earlier work. Mathewson, Spire and Milligan likewise investigated the liquidus and solidus curves in this region, but their results do not agree at all with those of H. Schenck and Hengler. Most important in connection with the present work is the fact that both of these sets of determinations of the liquidus and solidus curves are consistent or, at least, are not in marked disagreement with the wüstite area as given by R. Schenck and Dingmann. Pfeil determined the liquidus and solidus and likewise the extent of the wustite area in the solid state. His results are in violent disagreement with those of all the other investigators. He used chiefly thermal and microscopic methods. The results of all these investigators are plotted in Fig. 2, which also contains the results of the present work. It is evident that the present work agrees much better with Pfeil's results than with the others.

The few investigations of this range of iron oxides in which X-ray methods were used have been discussed in the earlier article already mentioned.

### MATERIAL AND METHODS

General details on these two topics and analytical methods were given in the earlier article. One of the oxides there described was used throughout the present work. It was made by tightly packing Fe<sub>2</sub>O<sub>3</sub>, prepared by igniting ferrous oxalate, in a large covered Armco iron cylinder and heating this slowly in a high-frequency furnace until the oxide layer that formed on the outside of the cylinder melted and ran down the sides; the material inside the cylinder melted under this treatment. It analyzed 76.15 per cent Fe, 0.018 per cent SiO<sub>2</sub> and 0.04 per cent S.<sup>9</sup>

This oxide was ground to pass 200 mesh and mixed with hydrogen-reduced iron or Fe<sub>2</sub>O<sub>3</sub> from the oxalate, to secure the desired final compositions. All the subsequent annealings and sinterings were carried out in vacuo. The total iron content of each of the oxides is included in

<sup>8</sup> C. Benedicks and H. Löfquist: *Non-metallic Inclusions*, 61. New York, 1931. John Wiley & Sons

<sup>9</sup> The presence of sulfur was entirely unsuspected and was not discovered until all the other work had been done. It is not believed that the amount found would have any appreciable effect on the results reported.

Table 1. Annealing and sintering periods varied from a few hours at the higher temperatures to several days at low temperatures. One of the two mixtures with excess iron (No. 9) was incased in thin platinum foil, sintered at 1031° C. and quenched. After grinding, part was reserved for chemical and the X-ray analyses and the remainder was divided into portions, each of which was wrapped in platinum foil, annealed at a desired temperature and quenched. After the sintering process this sample contained 77.4 per cent Fe. The second mixture (No. 13) was placed in an Armco iron cylinder and heated up to 1420° C. and quenched. At this temperature the oxide had melted, perhaps not completely but sufficiently to run to the lower portion of the horizontal cylinder. This

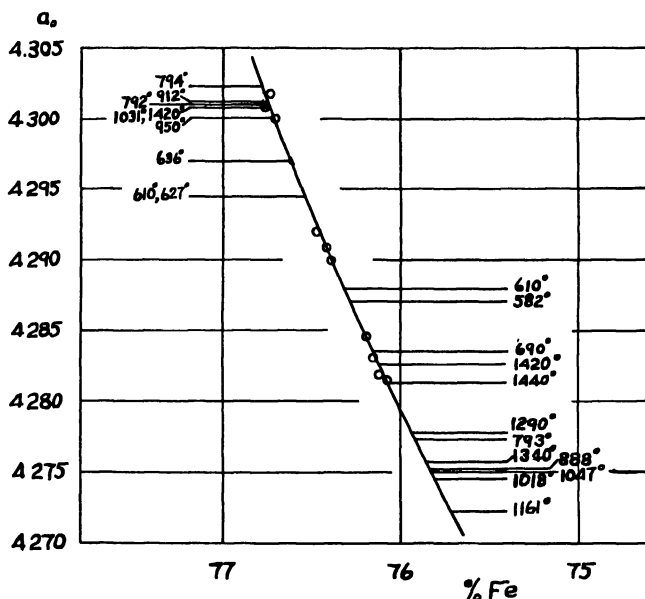


FIG. 1.—EXPERIMENTAL RESULTS OF INVESTIGATION.

oxide contained 79.9 per cent Fe. Small lumps of it were placed in small Armco iron cylinders and were then annealed and quenched from different temperatures. Separate portions of the melted material were reserved for chemical and X-ray analyses.

The oxides containing excess magnetite were prepared by similar methods, but platinum was the only material that could be used in contact with the oxides. In no case did these oxides melt even at 1440° C. It was very difficult to obtain equilibrium on this side of the system; the wüstite phase seems to take on oxygen from magnetite only at a slow rate. No oxide with a lattice constant smaller than that of the 1176° C. oxide was ever obtained, but films, showing magnetite lines and yet yielding lattice constants so large as to correspond to compositions well

within the wüstite area, were obtained in several instances. For this reason, particular care was exercised in determining the points above 1200° C., which indicate retrograde solubility. The oxide quenched from 1290° C. was held at this temperature for 18 hr. The oxides quenched from still higher temperatures were heated very slowly to these maximum temperatures and held there for 15 to 60 min. before quenching.

From the above it will be seen that the two-phase alloys actually used for the X-ray analysis fall into two groups: (1) Alloys quenched from the

TABLE 1.—*Limiting Compositions of Wüstite Area*

Iron Side					Magnetite Side				
Oxide No.	Total Fe in Oxide, Per Cent	Annealing Temp., Deg. C.	Lattice Constant $a$ , Å	Equilibrium Percentage Fe in Wüstite	Oxide No.	Total Fe in Oxide, Per Cent	Annealing Temp., Deg. C.	Lattice Constant $a$ , Å	Equilibrium Percentage Fe in Wüstite
9	77.4	610	4.2946	76.54	12	74.1	582	4.2871	76.29
13	79.9	627	4.2944	76.54	10	75.1	610	4.2879	76.32
13	79.9	686	4.2969	76.62	15	74.6	690	4.2835	76.16
13	79.9	793	4.3010	76.75	12	74.1	793	4.2772	75.91
9	77.4	794	4.3023	76.79	12	74.1	888	4.2752	75.83
	Poor film								
9	77.4	912	4.3012	76.75	14	74.3	1018	4.2745	75.81
13	79.9	950	4.3001	76.72	12	74.1	1047	4.2751	75.83
9	77.4	1031*	4.3009	76.74	14	74.3	1176*	4.2722	75.72
13	79.9	1420*	4.3008	76.74	16	74.2	1290	4.2777	75.94
					10	75.1	1340	4.2757	75.86
					12	74.1	1420*	4.2826	76.12
					16	74.2	1440*	4.2813	76.07

highest temperatures to which they had been exposed and the resulting material as such X-rayed (temperatures indicated by an asterisk in Table 1); and (2) alloys prepared from these high-temperature oxides by annealing for suitable periods at lower temperatures. The only cases not adequately described by this statement are alloy No. 10 at 610°, which was prepared from material sintered at 1033°, and No. 10 at 1315°, which was the same sinter heat-treated at the higher temperature. Alloys 14 and 15 were both sintered at 1161°. These differences in methods of preparation are particularly important on the magnetite side, for by this means the final values were in some cases reached by the precipitation and in others by the solution of magnetite.

The heat treatments were carried out in wire-wound tube furnaces. The oxide contained in a platinum foil wrapping or in an Armco iron cylinder was sealed into evacuated quartz tubes. For temperatures below 1100° C., the end of a calibrated Pt-PtRh thermocouple was placed in contact with the sample tube. For the higher temperatures a calibrated optical pyrometer was sighted on the end of the sample tube. In some cases, at these high temperatures, it was necessary to inclose the quartz tube in an outer protecting tube in which cases the pyrometer

was sighted on the protecting tube. For the temperature above  $1200^{\circ}\text{C}$ . either a platinum ribbon or a tungsten-wound furnace was used. The heating always took place slowly, so there was ample opportunity for temperature equilibrium to be attained. It is estimated that the temperatures measured with the thermocouple are correct within  $\pm 2^{\circ}\text{C}$ . and those with the optical pyrometer within  $\pm 10^{\circ}\text{C}$ .

The X-ray cameras were of the type designed by Phragmén on the Bohlin principle.<sup>10</sup> Radiation from an iron target was used. Fig. 1 shows that the lattice constant of wüstite changes at the rate of  $0.003\text{\AA}$  for each 0.1 per cent Fe. When sharp lines are secured from such a simple cubic structure it is easy to check the measurements to within less than  $\pm 0.001\text{\AA}$ , corresponding to 0.03 per cent Fe. On the iron side of the wüstite area, accuracy of this order was easily attained. On this side the average deviation of the observed points from the curve drawn in Fig. 2 is less than  $\pm 0.02$  per cent Fe.

On the magnetite side considerable difficulty was encountered in reaching equilibrium and the error due to this factor is, of course, included in the total. Since the lattice constant of wüstite changes so rapidly with composition, the X-ray analysis is a very sensitive test on this point. It was important therefore to approach equilibrium compositions from both directions, as noted above. Owing to this factor, the lines on the X-ray films were always rather diffuse and difficult to measure. The maximum error in determining this solubility line on the diagram is therefore considerably higher than on the iron side, but certainly does not exceed  $\pm 0.1$  per cent Fe. The average deviation of the observed 12 points from the curve as drawn in Fig. 2 is  $\pm 0.05$  per cent Fe.

## RESULTS AND DISCUSSION

The results of the present investigation are summarized in Figs. 1 and 2 and Table 1. In Fig. 1 the change of lattice parameter is plotted as a function of the composition, these results being taken from the previous publication, and the lattice parameters of the wüstite phase when in equilibrium with the neighboring phase at various temperatures are indicated. Fig. 2 contains not only the compositions thus obtained and plotted in the usual way as functions of temperature, but also the results of the three other investigations cited above.

On the high-iron side of the wüstite area, the most striking fact is that from  $800^{\circ}$  up to the highest temperature at which solid wüstite can exist the equilibrium composition of this phase is constant. At the highest temperature recorded, this alloy, which contained 79.9 per cent Fe, was largely in the molten state. An alloy containing 76.75 per cent Fe therefore contains the highest concentration of iron possible in wüstite.<sup>11</sup>

<sup>10</sup> A. Westgren: *Trans. A. I. M. E.* (1931) **93**, Inst. of Metals Div., 13.

<sup>11</sup> This point at  $1420^{\circ}$  is distinguished on Fig. 2 by a double circle to indicate that it may be shifted up or down as later determinations of the solidus curve may necessitate.

The compound  $\text{FeO}$ , therefore, does not occur pure in the iron-oxygen system. This result makes it impossible to accept the thermal diagrams for the wüstite area proposed by Benedicks and Lofquist<sup>12</sup> and by Ralston.<sup>13</sup> On both these diagrams the wüstite area at its maximum width extends only from 77 to 78 per cent Fe, and therefore lies entirely outside the range found by Pfeil and in the present investigation. The discussion of the wüstite area in these publications by Benedicks and Lofquist and Ralston was considerably influenced by the idea, which to a large extent was justified by the evidence available at the time each was written, that a single-phase oxide having the theoretical composition of  $\text{FeO}$  must exist. The present writers' unsuccessful attempts to prepare this compound were described in the previous article. The agreement between the limiting value of 76.9 per cent Fe found by Pfeil and that of 76.75 per cent reported here is about as close as can be expected, considering the difference in the methods used, but the lower value is deemed to be the more exact.

Below  $800^\circ \text{C}$ . the shape of the curve differs radically from that found by Pfeil. There can be no doubt, however, that the curvature found in the present work actually exists, as the change in the lattice parameter is very marked. The break at about  $800^\circ$  may have some relation to the  $A_3$  transformation. Ralston<sup>14</sup> on the basis of the earlier results of R. Schenck and Dingmann gives a diagram showing the  $A_3$  point lowered to about  $720^\circ$  by the presence of oxygen. These authors in a later paper<sup>15</sup> withdrew the data on which this diagram was based. H. Schenck and Hengler found no important change in the temperature of the  $A_3$  transformation due to oxygen. While the identification of the  $800^\circ$  break in the curve with the transformation of  $\alpha$  to  $\gamma$  iron may still be a possibility, it is not considered to be definitely established.

It has already been noted that the experimental difficulties on the magnetite side of the area were considerably greater than on the iron side, and that the accuracy therefore is somewhat lower. The agreement with Pfeil's results is again about as good as may be expected over the range of his actual experimental investigation on the solid materials. The last temperature at which Pfeil observed the 75.5 per cent Fe alloy to be single phase was  $1150^\circ \text{C}$ ., the curve above that was drawn to be consistent with his interpretations of the thermal arrest points. It is above  $1150^\circ \text{C}$ . that the greatest differences in the two sets of results are observed. In this connection it may be stated that if the limit at  $1440^\circ$  is nearly 75 per cent, as given by Pfeil, the outer-

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<sup>12</sup> Reference of footnote 8, 56.

<sup>13</sup> Reference of footnote 2, 292.

<sup>14</sup> Reference of footnote 2, 290.

<sup>15</sup> R. Schenck and T. Dingmann: *Ztsch. anorg. Chem.* (1929) **182**, 97.

most doublet on the X-ray photographs would have been shifted beyond the range of the camera, while actually the lines shifted in the opposite direction above 1176° C. This result was entirely unexpected; much time was spent in the earlier investigation in trying to get points within the homogeneous range at lower iron concentrations by heat treatments at high temperatures followed by quenching. It is not believed that this result can be explained satisfactorily by assuming that the composition changed radically during cooling. The equilibrium compositions

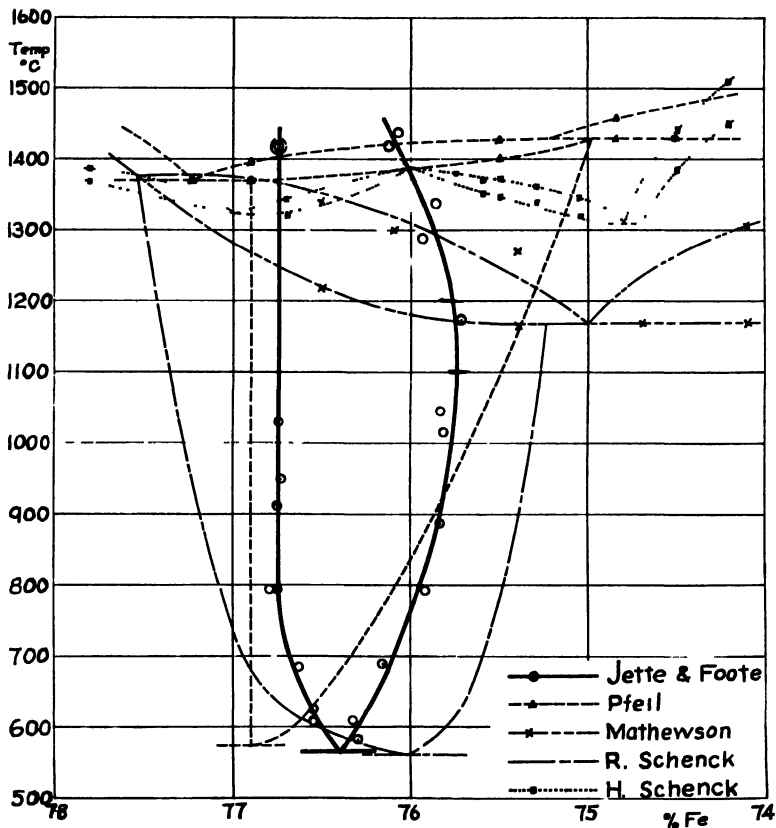


FIG. 2.—WÜSTITE RANGES IN THE Fe-O SYSTEM.

observed around 1400° C. are about the same as those at 700° C.; the samples were quite black within less than one minute after quenching and in one case the evacuated quartz tube broke during the quench, so that the cooling was even more rapid. If the composition had changed appreciably during the cooling, the lines on the photographs would have been spread over such wide areas as to have been practically obliterated. The lines observed, while somewhat diffuse in every case, did not permit such a conclusion. It is probable that the last three



temperatures are somewhat high. Oxide 16 showed signs of incipient melting at the highest temperature recorded.

Wherever possible, it is desirable to correlate the results of phase investigations in the solid state with the known liquidus and solidus curves. The three sets of these determinations reproduced in Fig. 2 show how unsatisfactory the situation is. The present writers have considerably more confidence in Pfeil's results than in the results of the other investigators. We wish, however, that Pfeil had included a few points in the range between 76 and 77 per cent Fe. It is possible, without taking too many liberties with Pfeil's results, to force an agreement between his liquidus and solidus and the present wüstite area, but as data for the critical region are lacking there is little to be gained in setting up another diagram. There are several experimental reasons, however, for believing that Pfeil's data are essentially correct. Alloy 16, which contained 74.2 per cent Fe, showed only incipient melting at 1440° C. (and that at only one end of the sample), which is essentially in agreement with Pfeil. According to Mathewson, Spire and Milligan, oxide 16 at 1290° should have been largely in the liquid state, and the oxides at the last three temperatures should have been entirely molten; there was no indication of melting except that already mentioned at 1440° C. According to H. Schenck and Hengler, oxides 12 and 16 at temperatures above 1290° C. should consist entirely of a solid solution phase based on the magnetite structure. Every photogram taken of oxides quenched from this region showed two phases and there was no measurable change in the positions of the magnetite lines. Further, according to these same authors, oxide 10 at 1340° C. should have been largely molten, which was not the case. Thus, in this general region, the results obtained in the present investigation are in agreement with Pfeil's determinations but not with those of other investigators.

The triple point at which iron, wüstite and magnetite are in equilibrium has been placed by various investigators between 560° and 575° C. The present results do not indicate this temperature with any great certainty, but several reasonable extrapolations of the two curves yielded values between these two limits, and probably this point should fall between 565° and 570°. The corresponding composition was in any case very close to 76.40 per cent Fe.

#### SUMMARY

The homogeneity limits of the wüstite solid solutions have been determined at various temperatures and the results expressed in a diagram. The results are in reasonably good agreement with those previously found by Pfeil, but differ radically from those of other investigators. The point at which wüstite decomposes into iron and magnetite is found to be at 76.4 per cent Fe and between 565° and 570° C. The compound FeO does not occur in the iron-oxygen system

## DISCUSSION

(Robert S. Archer presiding)

G. MÄNING, Berlin, Germany.—It seems that there are several cases of mixed crystals in which a law of substitution similar to that in the case of wüstite is to be assumed; as, for example, in cuprous oxide and in rock salt under the influence of ultraviolet light. In these cases a simple migration of one of the constituents must be assumed instead of substitution and therefore the existence of voids in the space lattice not occupied by an atom, where the atom should be. It seems necessary therefore to deal today with three kinds of mixed crystals—the substitutional, the interstitial, and the new kind that has not yet been named.

In this connection I want to ask Dr. Jette why he does not simply say that the iron atom is alone traveling in the space lattice instead of supposing a substitutional mechanism, as both views would agree with his results.

C. H. MATHEWSON, New Haven, Conn. (written discussion)—It is of interest to consider the bearing of Jette and Foote's results on the general configuration of the

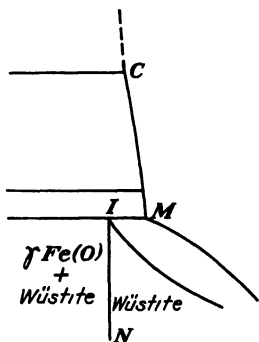


FIG. 3

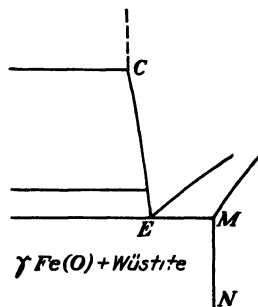


FIG. 4.

iron-oxygen constitutional diagram in the concentration region, Fe(O)-wüstite. If the diagram in this region exists in the form of Fig. 3, chemical analysis of an alloy *C* quenched close to *M* and chemically treated to remove free iron (separated along *CM*) would give the point *M* and would place the wüstite boundary curve *IN* at lower oxygen concentrations. If we regard the experimental determination of *M*, 77.0 per cent Fe, given by Mathewson, Spire, and Milligan<sup>16</sup> and the determination of *IN* by Jette and Foote, 76.7 per cent Fe, as substantially correct, the situation shown in Fig. 3 becomes impossible, because *IN* would be placed to the right of *M*. It might, however, be assumed that these concentrations are practically coincident, with solidus and liquidus meeting at *M* or *I*.

The latter is the construction adopted by H. Schenck and E. Hengler<sup>17</sup> with a further merging of these curves at a minimum and then again at a maximum, which thereupon drops to a eutectic minimum with the neighboring magnetic phase; an unusual condition that will require ample confirmation if it is to be generally accepted.

The construction shown by Mathewson, Spire and Milligan in 1931 (*op. cit.*), according to which solidus and liquidus curves arranged as in Fig. 3 drop to a eutectic

<sup>16</sup> Reference of footnote 4.

<sup>17</sup> Reference of footnote 3.

horizontal below 1200° C. can no longer be entertained, as Pfeil, H. Schenck and Hengler, and now Jette and Foote have definitely observed that mixtures in this range of concentration remain solid at temperatures far above this. It thus appears certain that the thermal data in question are unreliable, probably owing to the use of small thermocouple wires in reactive melts and the rapid cooling that was necessary under the existing conditions.

If the constitutional diagram in the Fe(O)-wüstite region exists in the form of Fig. 4, chemical analysis of an alloy *C*, cooled to *E* and quenched when frozen will give the point *M*, provided structurally free iron is chemically removed before the analysis. If, as before, we assume that Jette and Foote's left-hand boundary of wüstite is essentially correct, and if the experimental technique of determining this *M* point is likewise reliable, the point should lie on the boundary in question, *MN*. Actually, the experimentally determined *M* point, according to Mathewson, Spire and Milligan, is at 77.0 per cent Fe, and the Jette and Foote boundary in this region is at 76.7 per cent Fe, a very good agreement, considering the totally different nature of the two methods here compared.

The eutectic point *E*, according to Pfeil's analysis<sup>18</sup> of an alloy that he considered structurally pure eutectic, is located at 77.2 per cent Fe. The eutectic temperature, 1370° C., must be taken from Rosenhain, Tritton and Hanson's<sup>19</sup> thermal determination of the oxide arrest.

This critique, in my opinion, offers the best possible interpretation of the iron-oxygen diagram in the concentration region thus considered. Pfeil's results, as stated by Jette and Foote, seem to be the most satisfactory, but some further experimental work should be conducted in order to determine positively the character of the liquidus and solidus curves above the wüstite region and further along towards the concentration of the pure compound, magnetite.

It is disturbing to learn that the wüstite boundary determined by precision measurements of lattice parameter vs. concentration (with temp. correlation) fails so utterly to coincide with the boundary determined by R. Schenck and collaborators,<sup>20</sup> the latter apparently checked recently by H. Schenck and E. Hengler,<sup>21</sup> by (indirect) vapor-pressure measurements vs. concentration at different temperatures. It will be recalled that the question of the solubility of oxygen in ferrite gave rise to a rather lengthy history of investigation by R. Schenck and others following a critical discussion by Benedicks and Lofquist<sup>22</sup> in 1928 of the troublesome errors likely to occur in this form of experimentation. The value originally determined, about 2 per cent of oxygen at 700° C., wholly out of harmony with the metallographic evidence, was later reduced by persistent experimentation to about 0.1 per cent, where it may be said to stand as a maximum value in this temperature region at the present time.

The clean-cut and plausible results of the present investigation will probably strengthen a disposition to rely principally on thermal determinations supported by microstructural and X-ray work for the solution of troublesome constitutional diagrams.

A. ST. JOHN, New York, N. Y.—Was there any evidence of superlattice structure in the X-ray data on the FeO?

<sup>18</sup> L. B. Pfeil: *Jnl. Iron and Steel Inst.* (1931) **123**, 237.

<sup>19</sup> R. Schenck and collaborators: *Ztsch. anorg. Chem.* (1927) **166**, 113; (1928) **171**, 239; (1929) **182**, 97.

<sup>20</sup> Reference of footnote 19.

<sup>21</sup> Reference of footnote 3.

<sup>22</sup> C. Benedicks and H. Lofquist: *Ztsch. anorg. Chem.* (1928) **171**, 231.

E. R. JETTE.—No. We have examined those alloys at both ends of the homogeneous range by the Debye method, looking for that, and have not found it. That is rather important if a large superlattice is assumed, in which case it is possible to assume substitution of  $\text{Fe}_2\text{O}_3$ .

G. HAGG, Stockholm, Sweden (written discussion) —This paper shows the value of the X-ray methods in determinations of the extensions of homogeneity ranges, and the metallurgists ought to be indebted to the authors for their successful application of these methods to the FeO problem.

In their introduction the authors draw attention to an earlier paper, in which they have arrived at the conclusion that the excess of oxygen in the solid solutions in question is caused by a substitution of FeO groups in the ideal unit cell of FeO, by oxygen atoms. The authors consider the FeO lattice to be of the ionic type and that, consequently, the excess in negative charge effected by this substitution is balanced by a partial oxidation of ferrous iron to ferric iron.

The writer has recently called attention to a phenomenon, which seems to be of a rather analogous character, though its explanation was—at least formally—given in a slightly different form.<sup>23</sup> By means of X-ray measurements, compared with density values, it could be shown that when pyrrhotite contains more sulfur than corresponding to the formula FeS, the excess of sulfur is caused by a number of vacant positions in the iron lattice. The possibility of vacant positions makes possible a new type of phases with variable composition, for which the name "subtraction type" (cf. the hitherto known addition and substitution types of solid solutions) might be suggested.

In regard to the iron sulfides, there seemed not to exist any cause for the assumption of a complex substitution, and as the FeS lattice is probably nonionic, the appearance of vacant iron positions did not necessarily give rise to difficulties in the shape of unequal electrical charges.

In the wustite solid solutions, the assumption of any complex substitution, although *formally* not incorrect, seems quite as unnecessary as in the iron sulfides. The authors also admit the possibility of a subtraction type in stating that "such a substitution is equivalent to removing an iron atom (or ion)." A further cause for abandoning the conception of a substitution of FeO groups by oxygen is the non-existence of separate groups of FeO in the lattice.

The writer, consequently, would be inclined to consider the wustite solid solutions as an example of the subtraction type of solid solutions, where part of the iron atoms (or ions) have been subtracted from the ideal FeO lattice, thus causing vacant positions to appear. Whether the subtraction of iron must be accompanied by a partial oxidation of remaining atoms depends on the type of the FeO structure. The evidence of FeO being an ionic compound is not strong, and several facts (electrical conductivity, etc.) are in favor of a more or less metallic character. In the latter case, variations of the composition do not necessitate any displacement of the electric charges within the structure.

L. B. PREIL, Birmingham, England (written discussion) —The iron-oxygen system is of the greatest technical importance, and is worthy of the most detailed study. The paper by Messrs. Jette and Foote throws valuable additional light on the iron-oxygen equilibrium diagram. It may appear to some a matter merely of academic interest whether there be a eutectic between FeO and  $\text{Fe}_2\text{O}_3$ , or whether FeO has any real existence, but these points are of definite importance in connection with scaling problems, and in connection with blast-furnace reactions. In another direction also

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<sup>23</sup> *Nature* (1933) **131**, 167.

the iron-oxygen equilibrium diagram is of importance; *viz.*, with respect to the nature and constitution of inclusions in steel ingots, a subject that has received close attention in recent years.

I am gratified to find that Messrs. Jette and Foote, using the X-ray method, have confirmed that FeO does not exist, and also that there is no low-melting-point mixture in the range FeO to Fe<sub>3</sub>O<sub>4</sub>. The phase field of wüstite found by the authors differs in some respects from that which I found by microscopical examination, and I would like to ask the authors whether they are completely satisfied that the quenching operations which they employed were sufficiently drastic to prevent phase changes. In my experience the precipitation of magnetite from oxygen-rich wüstite could be prevented only by extremely rapid quenching. I found it necessary to carry out the heat treatment in a vacuum furnace and to allow a rush of ice water through the furnace so that the specimen was very drastically quenched.

In specimens containing less than about 75.5 per cent iron, a troostite-like structure was frequently observed after quenching, and I am inclined to the view that the structure resulted from the presence of an extremely finely divided precipitate of magnetite. It appears to me likely that the inoculating effect of such a precipitate might lead to a lower oxygen content in the residual wüstite than that of homogeneous samples of lower average oxygen content. The evidence obtained by the authors of homogeneity in the wüstite in the specimens from which they deduced retrograde solubility may have resulted from the highly dispersed nature of the magnetite precipitated during cooling, combined with the inoculating effect of the magnetite particles and the rapid rate at which diffusion occurs in wüstite.

The decreasing solubility of iron in wüstite found by the authors over the temperature range 570° to 750°, and which led them to select 76.4 per cent iron as the eutectoid composition, is of great interest. I found that specimens containing 76.6 and 76.7 per cent contained an excess of magnetite over the eutectoid composition, and it is difficult to appreciate the cause of the difference between the two sets of experimental results.

E. R. JETTE and F. FOOTE (written discussion).—The question of whether the structure of these solid solutions should be considered as complex substitution or as "subtraction" solid solution, as raised by Dr. Hagg and Dr. Masing, is an important one, even though from one point of view it is a purely formal matter. This question was given more detailed consideration in our earlier paper<sup>24</sup> which Dr. Hagg and Dr. Masing had not had the opportunity of seeing before their comments were made. The particular reason for expressing the results as a substitution of oxygen for an FeO group was that the simplest way of correlating the measurements of the lattice constants with the densities was to consider a lattice made up of FeO and O. It was clearly recognized that this type of substitution was equivalent to removing iron from the lattice, and it was shown, further, that the number of unit cells per gram of iron actually increased as the iron content of the oxide decreased. We are actually more in favor of considering the phenomenon in this way than as a substitution of FeO by O. We are also ready to accept Dr. Hagg's suggestion that this type of solid solution be called the "subtraction type."

At the time of writing, Dr. Hagg's work was unknown to us. While we suspected, in view of the difficulty in preparing pure FeS, that the phenomenon might be more common than is generally supposed, we preferred to be cautious, since these oxides represented the first case that had been thoroughly investigated. The difficulty of understanding the sharpness of X-ray diffraction lines, which arises in connection with metallic solid solutions, where the lattice dimensions are changed by the presence

<sup>24</sup> Reference of footnote 1.

of atoms of different sizes, is even greater when one (or more) of the prominent locations in a comparatively simple lattice is not occupied at all.

The evidence as to the ionic nature of the wustite lattice comes not only from intensity calculations but also from considerations of atomic and ionic radii. In addition, there is definite chemical evidence (footnote 1) that part of the iron is in the ferric state even when wustite is saturated with iron and excess iron is present.

Dr. Pfeil raises the question of the adequacy of the heat treatment of the alloys and points out the necessity for drastic quenching. This is in accord with our own experience. On account of the small size of our samples, and the fact that they were comparatively open sintered structures that were more than 2 or 3 mm. thick, we believe that the quenching operation was adequate. As pointed out in the article, our best evidence that precipitation of magnetite did not take place to an extent sufficient to account for the difference between our solubility curve on the magnetite side and that found by Dr. Pfeil is in the character of the diffraction lines observed. The effect of change of composition on the position of the lines is so great that had precipitation of magnetite taken place sufficient to change the wustite composition by more than 0.1 per cent Fe, the separation of the  $\alpha$  doublet could not have been observed. For the same reason, if the change in composition had been as great as would be estimated from the difference between Dr. Pfeil's curve and our own, no lines would have been found at all. We are grateful that Dr. Pfeil has brought up this point. Whenever a two-phase specimen must be prepared at a high temperature and examined at room temperature, as with both the X-ray and microscopic methods, the question of whether the high-temperature situation has been retained at the low temperature can never be finally answered. It is well, therefore, to understand clearly the nature of the evidence upon which the conclusions are based.

We are also at a loss to explain the difference between the curves on the iron side of the wustite range. The change in lattice constant corresponding to an increase in oxygen concentration was very definite at temperatures below 700° but we do not feel competent to reinterpret Dr. Pfeil's microscopic examinations.

# A New Thermocouple for the Determination of Temperatures up to at Least 1800° C.\*

By G. R. FITTERER,† PITTSBURGH, PA.

(New York Meeting, February, 1933)

INVESTIGATORS in the field of temperature measurement have long sought a thermoelectric couple fulfilling the following requirements:

1. It should be useful up to and including high industrial temperatures; *i. e.*, 1000° to 1800° C.
2. Its thermoelectric variation with temperature should be linear and be maintained after heating to high temperatures for long periods of time.
3. It should be reproducible; *i. e.*, different couples of the same elements should have similar calibration curves.
4. Its thermoelectric power should be large so as to allow the industrial use of rugged recording instruments.
5. Chemical reactions with, and physical changes within the elements of the couple should not alter its calibration.

No thermocouple proposed to date exhibits simultaneously all of these characteristics, whereas the couple about to be described fulfills all requirements to a satisfactory degree.

## NEW THERMOELECTRIC MATERIALS

A thorough survey of the literature on thermoelectricity revealed that present-day thermocouples could not meet the specifications mentioned above because their thermoelements are metallic. Metals have a marked tendency to deteriorate chemically and their melting points limit their use to low temperatures. Refractory substances, however, are usually resistant to chemical attack and are quite stable at high temperatures. Hence a survey of refractory substances having thermoelectric possibilities was made. One class of thermocouples considered was that in which carbon and a carbide of some metal or nonmetal were the thermoelements.

Previous investigators neglected to study this field but certain recommendations were made by them for the use of couples in which carbon served as one element. These proposals are listed in Table 1. The couples suggested are unsatisfactory because of their low thermoelectric powers, the low melting points of their metallic elements, etc. The

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tungsten-carbon couple cannot be considered as a tungsten carbide-carbon couple, as agreed by its originators in the discussion of their paper, and progressive carburization of the tungsten during use arouses some doubt as to its stability and reproducibility.

### PRELIMINARY EXPERIMENTS ON CARBON-CARBIDE COUPLES

The possibilities of the carbon-carbide couples were apparent after the first experiments. Carbides of silicon, tungsten, molybdenum, chromium (as chromel), aluminum, titanium and zirconium were prepared in rod or wire form and used as thermoelements. The calibrations of some of these are given in Fig. 1.

Attention should be called to the difference between the calibration curves of the WC-C couple prepared by the author and the W-C couple referred to in Table 1. The difference between their curves, shown in Fig. 1, suggests that they are entirely different in nature. The carbon-silicon carbide couple presented by far the most striking characteristics of any studied by the author, and the remainder of this paper will be devoted to a discussion of its properties.

TABLE 1.—*Thermocouples in Which Carbon Serves as One Element*

TYPE OF COUPLE	THERMOELEMENT OTHER THAN CARBON
Carbon vs. carbon	Bonded carbon <sup>a</sup>
Carbon-noble metal	Platinum <sup>b,c</sup>
Carbon-noble metal	Gold <sup>b</sup>
Carbon-base metal	Copper <sup>d</sup>
Carbon-base metal	Nickel <sup>e</sup>
Carbon-base metal	Tungsten <sup>f</sup>

<sup>a</sup> W. H. Bristol: Thermocouples of Graphite. *Engineering* (1908) **86**, 37. U. S. Patent 885430.

H. Muraoka: Thermoelectric Powers of Various Forms of Carbon. *Wied. Ann.* (1881) **13**, 307.

C. C. Bidwell: Thermojunction of Carbon and Graphite. *Phys. Rev.* [3] (1914) **38**, 450-452.

<sup>b</sup> A. Bartoli and G. Papasogli: Thermoelectric Materials. *Nuovo Cimento* (1882) **12**, 181.

<sup>c</sup> J. Buchanan: On the Thermoelectric Position of Carbon. *Phil. Mag.* [5] (1885) **20**, 117.

M. LaRosa: Thermoelectric Effect of a Carbon-Platinum Couple. *Palermo Nuovo Cimento* (1916) **12**, 284-301.

<sup>d</sup> J. Weiss and J. Königsberger: The Thermoelectric Power of the Copper-Carbon Couple. *Phys. Ztsch.* (1909) **10**, 956.

<sup>e</sup> Anon.: A Thermoelectric Couple of Carbon and Nickel. *Stahl und Eisen* (1918) **38**, 1044; *Jnl. Soc. Chem. Ind.* (1918) **38**, 29A.

<sup>f</sup> H. L. Watson and H. Abrams: Thermoelectric Measurements of Temperatures Above 1500° C. *Trans. Amer. Electrochem. Soc.* (1928) **54**, 19.

W. F. Holbrook, C. C. Furnas and T. L. Joseph: Diffusion of Sulphur, Manganese, Phosphorus, Silicon, and Carbon through Molten Iron. *Ind. & Eng. Chem.* (1932) **24**, 993.



## THE SILICON CARBIDE-CARBON THERMOCOUPLE

*Preparation.*—A silicon carbide rod was run lengthwise through a carbon tube, as shown in Fig. 2. The tube was closed and rounded at one end. The hot junction was prepared by tightly fitting the silicon carbide rod into a socket on the inside of this closed end. Because of the large inside diameter of the tube, the two elements did not come in contact at any other point. This was insured by means of a split and tapered refractory ring, which separated the two at the open end of the tube. As

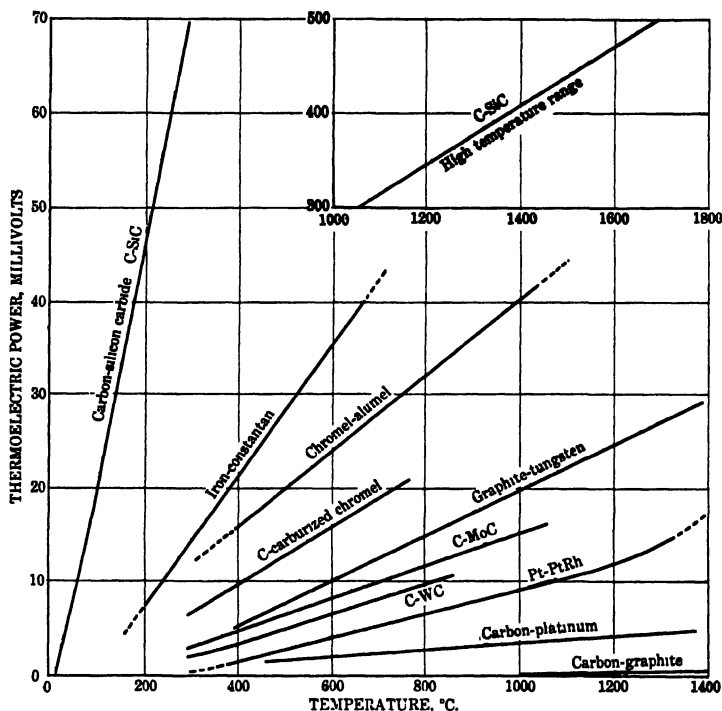


FIG. 1.—COMPARISON OF CARBON-CARBIDE THERMOCOUPLES WITH SOME OF THE MORE COMMON COUPLES USED TODAY.

shown in Fig. 2, cold junctions were made for both elements by means of water circulating through copper coils. Rubber tubing connected the two coils and only one inlet and one outlet were required.

*Calibration.*—The most satisfactory method used for the calibration of this new couple was to measure its thermoelectromotive force at temperatures determined simultaneously with a platinum-platinum rhodium thermocouple and an optical pyrometer, both of which were thoroughly standardized.

A special calibration tip of carbon was used (Fig. 3). The C-SiC junction (at B) was only  $\frac{1}{4}$  in. from the junction (at A) of the silica-

protected platinum-platinum rhodium couple. The optical pyrometer sighting wall (C) was  $\frac{5}{8}$ -in. from the C-SiC junction and possibly  $\frac{3}{4}$  in. from the platinum-platinum rhodium junction. These points (A, B and C) were centered in a high-frequency induction furnace by packing in lampblack. The furnace was heated to high temperatures and simultaneous readings taken on all three instruments during cooling. Six calibrations were made in this manner, the results of which are shown in Table 2 and Figs. 1 and 4. Two other calibrations were made in a different manner, and for the sake of brevity will not be discussed here.

*Discussion of Results.*—Calibration No. 8 was made entirely by comparison with the optical pyrometer, because the temperatures attained were far above the useful range of the platinum-platinum rhodium couple. This high temperature range is given in Table 2 as range No. 1. However, because of the greater accuracy of the platinum-platinum rhodium values as compared with optical pyrometer readings, most of the data obtained were for temperatures up to the useful limit of the standard couple.

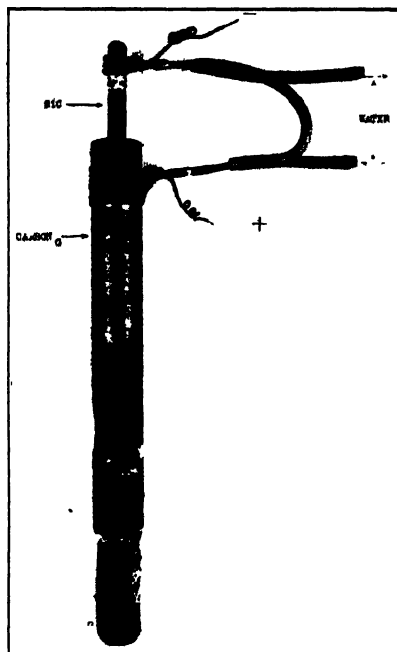


FIG. 2.—CARBON-SILICON CARBIDE THERMOCOUPLE.

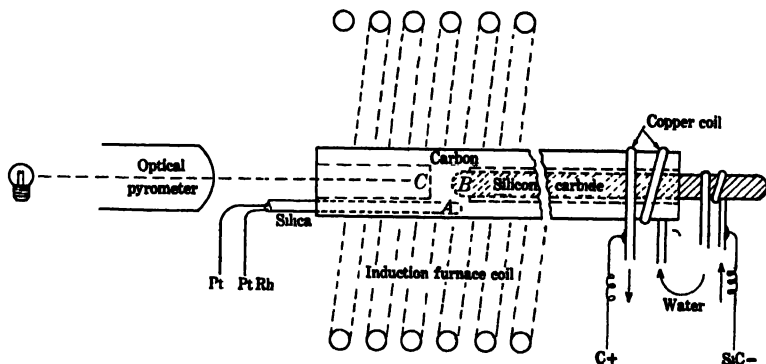


FIG. 3.—METHOD OF CALIBRATION OF C-SiC COUPLE.

Temperature ranges 2 to 8 inclusive are groups of similar C-SiC readings taken in different calibrations. These values have been grouped

together in this manner so as to facilitate comparison. Other values were obtained but the data are too voluminous to include herein. Many of the values not given in Table 2 have been plotted in Fig. 4. The first three optical pyrometer-C-SiC readings given in Table 2 have not

TABLE 2.—*Calibration of C-SiC Thermocouple*

Temperature Range No	Calibration No.	C-SiC, Mv.	Temperature, Deg C	
			According to Pt-PtRh Couple	According to Optical
1	8	508 0		1700
	8	483 6		1656
	8	480 6		1626
	8	476 0		1614
	8	471 9		1595
	8	465 8		1576
	8	456 0		1560
	8	451 2		1544
	8	446 8		1528
	8	442 8		1524
	8	438 3		1492
	8	433 8		1478
2	3	424 9	1455	1472
	6	424 9	1450	1471
	7	423 9	1445	1471
	8	424 9		1454
3	3	415 95	1420	1434
	5	417 7	1425	1440
	6	419 4	1430	1448
	7	419 5	1430	1454
	8	415 5		1422
4	3	405 5	1380	1388
	4	402 5	1355	1366
	5	404 5	1370	1364
	6	403 2	1360	1374
	7	402 5	1355	1370
	8	404 0		1374
5	3	392 0	1320	1325
	4	392 5	1322	1332
	7	392 5	1322	1332
	8	392 0		1321
6	3	385 95	1305	1310
	4	385 2	1300	1302
	6	380 4	1285	1294
	7	381 9	1290	1302
	8	388 6		1318
7	3	371 75	1267	1279
	5	369 7	1260	1273
	7	371 3	1264	1279
	8	370 3		1260
8	4	356 3	1217	1232
	5	356 1	1215	1231
	6	356 5	1215	1234
	7	353 6	1210	1221
	8	355 1		1225

been plotted in this figure but are in accordance with the calibration line.

The line has been drawn through the platinum-platinum rhodium temperatures and it may be seen that these values agree well with one another. Also, the optical pyrometer values are shown to be in good agreement with themselves and to form a parallel line to the platinum-platinum rhodium temperatures. This part of the curve is shown to have a slight curvature, whereas above or below this range it is practically a

straight line. Two calibrations not listed herein established the line down to room temperature. The equation for this line is

$$t^{\circ}\text{C.} = 50 + 3.32 (\text{mv.})$$

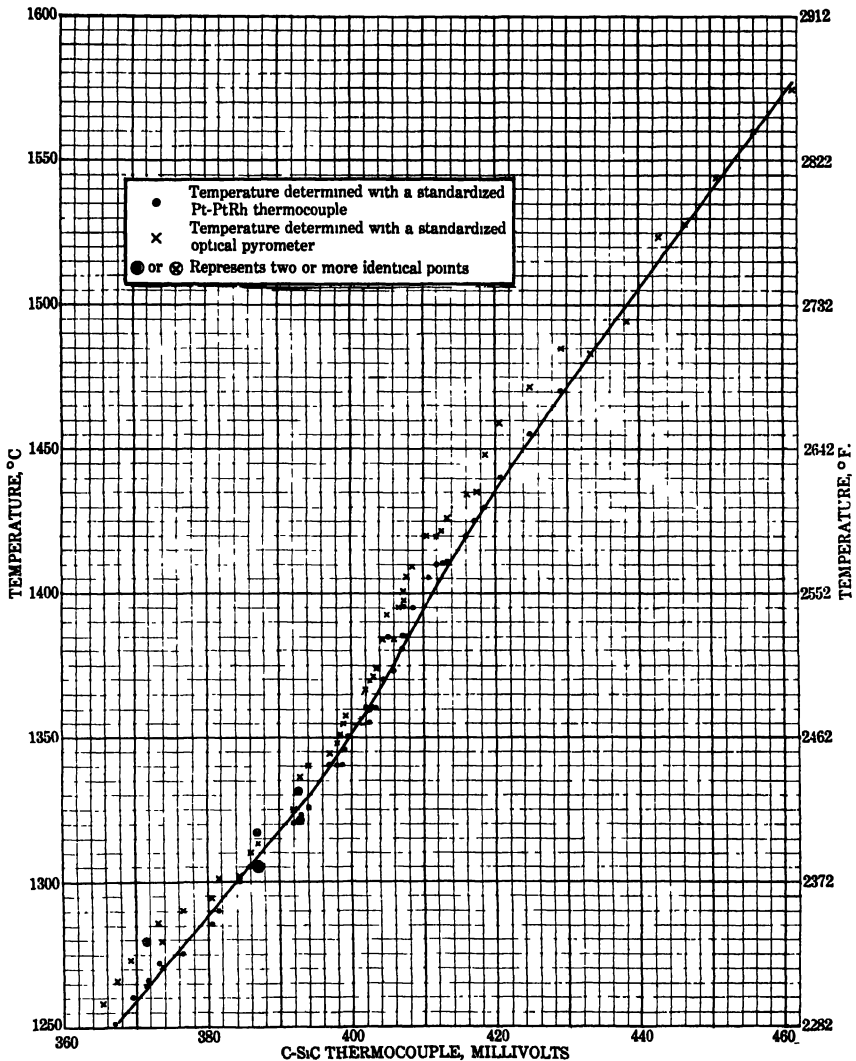


FIG 4—VALUES OBTAINED IN SIX CALIBRATIONS OF THE C-SiC THERMOCOUPLE.  
Curve has been drawn through the more accurate calibrations against the platinum-platinum rhodium couple.

wherein mv. is the millivolt reading of the C-SiC couple at any temperature.

*Thermoelectric Power.*—According to the above equation the slope of the calibration line is 3.32 degrees per millivolt or approximately 300

microvolts per degree Centigrade. This quantity is usually termed the thermoelectric power ( $H$ ) of the couple. One requirement of a useful thermocouple is large thermoelectric power, and that of the C-SiC couple ( $H = 300$ ) is the largest (to the author's knowledge) ever recorded. The thermoelectric powers and the temperature limitations of the more common couples may be compared with this by referring to Fig. 1. The power of the C-SiC couple is approximately 30 times that of the platinum-platinum rhodium couple, 7 times that of the chromel-alumel couple, and 5 times as large as the iron-constantan couple. The chief advantage of the high thermoelectric power of this couple is that stronger and yet just as accurate industrial recording instruments can be used.

*Reproducibility.*—Various couples prepared by the author and others using the same calibration method reproduced the calibrations shown in Figs. 1 and 4 within less than one per cent. Some divergence however has been reported by others using slightly different calibration methods. The difference reported by them amounted to as much as 4.25 per cent. The author does not believe that all of this difference was due to varied methods of calibration; probably it was largely due to the presence of some extraneous material such as silicon in the silicon carbide member. In the author's experiments it was found advisable to preheat the couples by running them back and forth through an induction furnace at 1500° to 1600° C. for at least  $\frac{1}{2}$  hr. In the near future further research work will be directed towards the study of these factors as well as the development of more accurate calibration methods.

*Cold-junction Characteristics.*—The water-cooling coils constituting the cold junctions as shown in Fig. 2 were placed in series with a flow meter and inlet and outlet thermometers. Observations were made with regard to the effect of the rate of flow on outlet temperatures and the effect of differences in inlet and outlet temperatures on the calibration of the couple. In all cases the effect was slight.

*Stability.*—As shown in Fig. 1, the maximum temperature to which the various couples may be conscientiously used are: C-SiC, at least 1700° to 1800° C.; Pt-PtRh, 1400° C.; chromel-alumel, 1100° C.; and iron-constantan, 700° C.

Both elements of the C-SiC couple are highly stable materials. The maximum temperature to which they may be subjected is unknown at the present time. It is probably somewhat below 2700° C.—the supposed melting point of silicon carbide. Carbon, of course, melts at a much higher temperature (3000° C.). Both elements are also highly resistant to chemical contamination so evident in metallic couples.

Carbon exists in two forms and a couple prepared from elements of each type exhibits a thermoelectric potential of 40 microvolts at 1400° C., as shown in Fig. 1. The potential of the C-SiC couple at 1400° C. is approximately 400,000 microvolts and the maximum effect of an allotropic transformation of carbon would be less than 0.01 per cent.

## INDUSTRIAL APPLICATIONS

*Determination of Liquid-steel Temperatures.*—Between the calibrations listed in Table 2, the temperatures of various liquid-steel baths were determined. The C-SiC couple was immersed in metal baths for long periods of time during each series of measurements, and it is pertinent that such heating at high temperatures did not affect the calibration of the couple as indicated by the manner in which the various calibrations checked one another. Whenever possible the temperatures were checked by a Pt-PtRh couple but in such cases low-temperature melts—cast iron, for instance—were studied so as not to destroy the Pt-PtRh couple.

Two 8-ft. couples have been prepared and calibrated for steel-plant use and some very interesting data have already been obtained. Pig-iron temperatures in the runner and open-hearth tapping temperatures have been measured, but will not be described herein. It has long been the hope of the steel manufacturer to measure open-hearth temperatures previous to tapping, and the author has already determined that proper use of this couple will produce highly satisfactory results. Temperature control in this regard could be extended to the tapping of each type of steel at a predetermined temperature interval above its melting point. Such control may be likened to the present practice of the "heat treater" who anneals or quenches each steel at a predetermined temperature interval above its critical point.

*Miscellaneous Applications.*—The usefulness of this couple is not limited to high temperatures, although the high-temperature industries will probably be the first to apply it to their processes. Industries pertaining to fuel, ceramics, nonferrous metals, and even cryogenic processes, should benefit by this development.

## ACKNOWLEDGMENT

The author is indebted to and wishes to express his appreciation of the assistance of Messrs. H. K. Griffin, P. G. Guest, M. B. Royer, Hyman Freeman and W. L. Barrett, who helped in many ways to make these tests successful.

## DISCUSSION

(George B. Waterhouse presiding)

L. RUMFORD, II, Kearny, N. J.—From what source of carborundum rod has the author obtained satisfactory material for the negative element of this thermocouple? If, for example, a standard Globar resistance unit was employed (the two ends of which differ in composition from the portion between the ends) were the two ends of the Globar unit broken off, or was the entire unit used?

G. R. FITTERER.—This couple as shown in the figure was used with a Globar element. You can break off both ends and it does not make much difference in the calibration.

L. RUMFORD, II.—I would be interested to know how many of these thermocouples you have constructed, Dr. Fitterer; how reproducible you have found the calibration of each thermocouple, and what agreement you have observed between the calibrations of different thermocouples?

G. R. FITTERER.—Up to this time about ten couples have been prepared, and the calibrations of the various couples were reproduced within about 1 per cent. A given couple reproduced its own calibration accurately after innumerable reheatings to high temperatures.

L. RUMFORD, II.—The description of your experiences with this thermocouple for open-hearth work is interesting. We have noted your suggestion to heat the thermocouple by putting it in the wicket of the furnace door before immersing it in the bath. Now, to what depth in the bath were you able to push the thermocouple's hot junction? Do you believe you can measure the temperature of the layer of molten steel that is close to the furnace bottom?

G. R. FITTERER.—I have immersed the couple about a foot into the hot metal. The couple is quite wieldy and buoyant when immersed in the slag or the metal. The slag-metal interface is easily detected by its much greater buoyancy in the metal. Hence the gas temperature may be determined during preheating. The couple may then be inserted in the slag and its temperature determined. The slag-metal interface may then be found, and the metal temperature found by deeper insertion. This entire process would not take more than 3 min.—2 min. for gas temperature; 30 sec. for slag and 30 sec. for metal temperatures.

L. RUMFORD, II.—Have you used this thermocouple for measuring the temperature of molten pig iron during a blast-furnace cast?

G. R. FITTERER.—Yes.

L. RUMFORD, II.—One would expect a graphite tube to last much longer in molten pig iron than in molten steel. What life did you obtain from the graphite tubes in the blast-furnace application?

G. R. FITTERER.—I can make this statement, that in one test in the blast furnace the couple was immersed about a foot into the stream for an hour and fifteen minutes. After it was taken out, the machine marks were still on the carbon.

L. RUMFORD, II.—Can you tell us, approximately, the temperature of the cold-junction cooling water that corresponds to the measurement used to make the calibration curves shown in your paper?

G. R. FITTERER.—Eighteen degrees Centigrade.

F. B. FOLEY, Philadelphia, Pa.—I noticed that you used the external element as the carbon. Would there be advantages of having the carborundum for the outside element and carbon for the inside?

G. R. FITTERER.—That is a very interesting point from this standpoint: In measuring the temperature of gases, the silicon carbide could be used for the outside element. Silicon carbide is highly resistant to all gases, even to oxygen at very high temperatures. It will form a thin film of silica on the outside and become resistant to further oxidation. A reversal of this couple with a silicon carbide tube and a carbon rod in the center would often be advantageous.

F. B. FOLEY.—What would be the disadvantage in case of metal temperature?

G. R. FITTERER.—In the case of iron temperature, the silicon carbide would dissolve rapidly into the metal.

F. B. FOLEY.—Do you require a very tight junction?

G. R. FITTERER.—There are several methods of getting a good junction. A  $\frac{3}{4}$ -in socket depth is usually sufficient.

J T. MACKENZIE, Birmingham, Ala.—It seems to me that the protective process that was developed in the foundry laboratory at the Bureau of Standards with the burned-on zirconia and clay coating might enable you to reduce the size of these units and greatly shorten the time necessary for reading. The time lag was what whipped the graphite-tungsten thermocouple, because you had to wrap it up in so much refractory that it was just too clumsy to use.

G. R. FITTERER —Mr MacKenzie, have you ever measured the lag from room temperature up to  $1000^{\circ}\text{C}$  with a platinum-platinum rhodium couple?

J T. MACKENZIE —We read temperatures in the foundry in every way with platinum-platinum rhodium.

G. R. FITTERER —How long does it take the platinum to come up?

J T. MACKENZIE —About 30 sec in a 1-in graphite tube

G. R. FITTERER —You have done better than I. I have found that time lag up to  $1000^{\circ}$  is approximately 30 seconds

J T. MACKENZIE - Of course, that is an immersion of approximately 18 in where the assembly is preheated by holding in the ladle during filling

D. J. MARTIN, Watertown, Mass (written discussion) —Dr. Fitterer was kind enough to give me detailed information concerning his silicon carbide vs carbon thermocouple several months ago. Since that time a thermocouple of these materials has been tested at the Watertown Arsenal for use in measuring the temperatures of molten steel in high-frequency induction furnaces.

The thermocouple used at the Watertown Arsenal is very similar to that which has just been described. The outside diameter of the carbon element is  $1\frac{1}{2}$  in. and the over-all length of the couple is 20 in. To lengthen the life of this couple a carbon tip was made as a separate unit, to screw on to the carbon rod. The tip can thus be replaced when it is dissolved away without rebuilding the couple. The tip used is 5 in long and is closed and rounded at one end. The silicon carbide rod is  $\frac{5}{8}$  in. in diameter. This couple was calibrated to  $1350^{\circ}\text{C}$ ., in a heat-treating furnace by checking against a platinum couple inserted in a hole drilled in the side of the carbon tip. Calibration was then continued to  $1610^{\circ}\text{C}$ ., in molten steel. The platinum couple, protected by a quartz tube, was placed in the bath beside the carbon couple. The results obtained gave a straight line of the following equation:

$$t^{\circ}\text{C.} = 80 + 3.29 (\text{mv.})$$

This equation is in close agreement with that obtained by Dr. Fitterer under different conditions and with a couple of different dimensions. The slopes of the two calibration curves differ by about 0.6 per cent. and the difference in temperature readings is about 1 per cent. (approximately  $15^{\circ}\text{C}$ .) for temperatures in the range from  $1400^{\circ}$  to  $1700^{\circ}\text{C}$ .



Two different silicon carbide rods and a number of carbon tips have been used with the couple. None of these changes have affected the relationship between temperature and electromotive force to any appreciable extent. The greatest difference from the above calibration amounted to but 10° C. Hence, the reproducibility of this couple will be a valuable factor in its favor.

In the application of this couple to the determination of liquid-steel temperatures, it must be admitted that the carbon at the hot junction will be dissolved to some extent in the steel bath. The amount of this deterioration will depend somewhat upon the relative dimensions of the couple. In the couple just described an immersion time of about 5 min. ate away the carbon tip to such an extent that it was reduced in size dangerously close to the point of exposing the silicon carbide rod. This period of time was sufficient for one or two readings, after which it was necessary to replace the carbon tip of the couple.

Dr. Fitterer should be congratulated for his work. With proper development, his thermocouple should fill what is now a very noticeable gap in the field of applied pyrometry.

C. H. HERTY, JR., Pittsburgh, Pa.—I would like to ask Dr. Fitterer two questions and make one suggestion along the lines Lieutenant Martin spoke of. In the first place, some three years ago when Mr. Gaines and I were working on liquid-steel temperatures we always got into trouble when we put an insulated couple into the furnace unless the heat was killed. My first question would be, what is the effect of boiling on this couple?

The second question is, have you done any work on low-carbon steels where the carbon tube would be dissolved much more rapidly than in a high carbon?

The suggestion I would have to make and at the same time ask a question with it, would be some sort of a clay graphite tube instead of a straight graphite for a resistance to corrosion of the couple as well as protection against boiling.

G. R. FITTERER.—In answer to Dr. Herty's first question, I frankly do not know just what effect the boiling has upon the temperature measurements. It has been my belief that there is sufficient heat capacity in an open-hearth furnace to displace the metal by boiling and obtain repeated contact. Thermal equilibrium is finally attained, which is satisfactory for measurement.

As far as the lowest carbon steel on which this has been used, one of the 8-ft. couples has been used in 0.26 per cent carbon steels with excellent results.

J. T. MacKENZIE.—What about the clay graphite?

G. R. FITTERER.—The clay graphite has interesting possibilities. That is something I have not had time to investigate.

P. H. BRACE, Pittsburgh, Pa.—Is it essential to use potentiometer methods to measure millivolts?

G. R. FITTERER.—As far as the potentiometer method vs. the low voltmeter method, the resistance of this couple is low enough so that good measurements can be made with a high-resistance voltmeter. The resistance of a 2-ft. couple at 25° C. is approximately  $4\frac{1}{2}$  to 5 ohms. This decreases with the increase of temperature to about 3 ohms at 1000° C.

H. H. LESTER, Watertown, Mass.—Did the depth of immersion have an important bearing on the millivolts?

G. R. FITTERER.—So far as I could find out, it did not have any. In one experiment I found no difference between measurements at 2 and 12 inches.

P. D. FOOTE, Pittsburgh, Pa. (written discussion).—Mr. Fitterer is to be congratulated for the excellent results he has accomplished with the silicon carbide-carbon thermocouple. The large e.m.f. and the constancy of calibration are most pleasantly surprising. The couple should have many uses in industry. One especially promising development may be opened by reversing the carbon and silicon carbide electrodes for use in an oxidizing atmosphere; under such conditions silicon carbide shows excellent resistance to deterioration.

G. R. FITTERER (written discussion).—I am particularly gratified to learn that Lieutenant Martin has so accurately checked the findings of my work. No doubt the peculiarities of induction-furnace practice offer some of the worst difficulties to the measurement of liquid-steel temperatures by this means. However, if the couple could in any way be preheated for a period of 2 min. at a high temperature, it would only be necessary to immerse the couple in the metal for a period of 30 seconds. The 5-min. period described by Lieutenant Martin would thus be reduced to 8 to 10 periods of 30 sec. duration, or 8 to 10 heats, after which the carbon tip could be replaced. Dr. Foote's vast experience in high-temperature measurements is probably partly responsible for his enthusiastic and hopeful suggestions as to the possibilities of this new thermocouple.



# INDEX

(NOTE. In this index the names of authors of papers and discussions and of men referred to are printed in SMALL CAPITALS, and the titles of papers in *italics* )

## A

- ABORN, R H AND BAIN, E C : *Discussion on Widmanstätten Structure in Iron-carbon Alloys*, 252
- ALLEN, R M : *Discussion on An Improved Nickel-chromium Hardened Chilled Cast Iron*, 70
- American Institute of Mining and Metallurgical Engineers. Institute of Metals Division, annual lecture, 1933, 6, 13  
officers and committees, 1932-33, 8  
officers and directors, 7
- Austenite. crystal upsetting process, 256

## B

- BAIN, E C AND ABORN, R H : *Discussion on Widmanstätten Structure in Iron-carbon Alloys*, 252
- BARRETT, C S, MEHL, R F AND SMITH, D W : *Studies upon the Widmanstätten Structure, IV --The Iron-carbon Alloys*, 215
- BELAEV, N T : *Discussion on Widmanstätten Structure in Iron-carbon Alloys*, 250
- BENEDICKS, C : *Discussion on Analyses of Inclusions in High-carbon Tool Steels*, 195
- BLOOD, R. M : *Discussion on Effect of Small Percentages of Chromium on Cast Iron*, 49
- BRACE, P. H : *Discussions on Analyses of Inclusions in High-carbon Tool Steels*, 193  
*on A New Thermocouple for the Determination of Temperatures up to at Least 1800° C*, 300  
*on Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 180, 181
- BUERGER, M J. : *Discussion on X-ray Study of Iron-silicon Alloys*, 274
- BURGESS, C O : *Effect of Small Percentages of Chromium on the Quality of Cast Iron*, 37; *Discussion*, 51

## C

- Cast iron: chilled, structure, terminology, 71, 73  
chromium effect, bibliography, 47  
effect of small percentages on casting characteristics, hardness vs. section, strength, machinability, heat resistance and structure, 37

- Cast iron: growth, effect of chromium, 48  
nickel-chromium, hardened chilled applications, 63, 67, 70  
hardness, 69, 71, 73, 75  
influence of auxiliary elements, 57, 68  
physical properties, 53  
physical properties compared with those of plain iron, 60  
production, 53  
quality, effect of small percentages of chromium, 37
- Cobalt-chromium alloy: for high-speed tools, hot-hardness, experimental study, 98, 114, 125
- Coke. ash variations, effect on pig-iron analyses, 28
- COMSTOCK, G F : *Discussion on Effect of Small Percentages of Chromium on the Quality of Cast Iron*, 47
- Copper steel See Steel
- CRAFTS, W, EGAN, J. J AND KINZEL, A B : *Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 169, *Discussion*, 183
- Creep of metals: relation to hot-hardness, 128
- Crystallography crystal upsetting process in austenite, 256

## D

- DAY, R O AND WISSLER, W. A : *Discussion on Hot-hardness of High-speed Steels and Related Alloys*, 125
- DEAN, R S : *Discussion on Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 178
- DE FOREST, A. V. : *Discussion on Precipitation-hardening of Copper Steels*, 165
- DIGGES, T G. : *Discussion on Hot-hardness of High-speed Steels and Related Alloys*, 128

## E

- EGAN, J. J., CRAFTS, W AND KINZEL, A. B : *Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 169; *Discussion*, 183
- EMMONS, J. V : *Discussion on Hot-hardness of High-speed Steels and Related Alloys* 125

## F

- Facing metals *See* Hard-coating Alloys
- FITTERER, G. R.: *A New Thermocouple for the Determination of Temperatures up to at Least 1800° C*, 290; *Discussion*, 297, *et seq.*
- Discussion on Analyses of Inclusions in High-carbon Tool Steels*, 193
- FOLEY, F. B.: *Discussion on A New Thermocouple for the Determination of Temperatures up to at Least 1800° C*, 298
- FOOTE, F. AND JETTE, E. R.: *A Study of the Homogeneity Limits of Wustite (FeO) by X-ray Methods*, 276
- FOOTE, P. D.: *Discussion on A New Thermocouple for the Determination of Temperatures up to at Least 1800° C*, 301
- FRANK, R. H.: *Discussion on Hot-hardness of High-speed Steels and Related Alloys*, 127

## G

- GERMAN, H. M.: *Discussion on Properties of Low-carbon Medium-chromium Steels of the Air-hardening Type*, 86
- GILLET, H. W.: *Discussion on Precipitation-hardening of Copper Steels*, 165, 168
- GREINER, E. S. AND JETTE, E. R.: *An X-ray Study of Iron-silicon Alloys Containing 0 to 15 Per Cent Silicon*, 259
- GROVE, H. A. AND HARDER, O. E.: *Hot-hardness of High-speed Steels and Related Alloys*, 88

## H

- HAGG, G.: *Discussion on Homogeneity Limits of Wustite by X-ray Methods*, 287
- HALL, J. H.: *Discussion on An Improved Nickel-chromium Hardened Chilled Cast Iron*, 69
- Hard-coating alloys: hot-hardness, experimental study, 98, 114, 127
- HARDER, O. E.: *Discussions on Hot-hardness of High-speed Steels and Related Alloys*, 131  
*on Intermediate Phases of the Iron-tungsten System*, 212
- HARDER, O. E. AND GROVE, H. A.: *Hot-hardness of High-speed Steels and Related Alloys*, 88
- HARDING, E. W.: *Discussion on An Improved Nickel-chromium Hardened Chilled Cast Iron*, 65
- Hardness, hot, relation to creep in metals, 128
- Haynes Stellite. *See* Stellite
- HERTY, C. H. JR.: *Discussions on A New Thermocouple for the Determination of Temperatures up to at Least 1800° C*, 300  
*on Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 176, 179
- High-speed tools *See* Cobalt-chromium, Steel, Stellite, etc

Howe Memorial Lecture: list of lecturers, 6  
tenth (WATERHOUSE), 13

HUDSON, R. P.: *Discussion on Effect of Variations in Coke Ash on Pig-iron Analyses*, 36

## I

- Inclusions in steel *See* Steel.
- Institute of Metals Division: annual lecture, 7, 13  
officers and committees, 1932-33, 8
- Iodine method of oxide analysis. *See* Steel-making
- Iron, cast *See* Cast Iron
- pig *See* Pig Iron
- Iron-carbon alloys: Widmanstätten structure, 215  
Widmanstätten figures, scope of term, 252  
256
- Iron-oxygen alloys: wüstite *See* Wüstite
- Iron-silicon alloys: Si 0-15 per cent, X-ray study, 259
- Iron-tungsten alloys, intermediate phases, 198

## J

- JETTE, E. R.: *Discussions on Homogeneity Limits of Wustite by X-ray Methods*, 287  
*on X-ray Study of Iron-silicon Alloys*, 274, 275
- JETTE, E. R. AND FOOTE, F.: *A Study of the Homogeneity Limits of Wustite (FeO) by X-ray Methods*, 276, *Discussion*, 288
- JETTE, E. R. AND GREINER, E. S.: *An X-ray Study of Iron-silicon Alloys Containing 0 to 15 Per Cent Silicon*, 259
- JOB, R.: *Discussion on Effect of Small Percentages of Chromium on the Quality of Cast Iron*, 48
- JOHNSON, H. W.: *Effect of Variations in Coke Ash on Pig-iron Analyses*, 28
- JOHNSTON, J.: *Discussion on Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 179

## K

- KINEEL, A. B.: *Discussions on Analyses of Inclusions in High-carbon Tool Steels*, 192  
*on Hot-hardness of High-speed Steels and Related Alloys*, 130, 131  
*on Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 177 *et seq.*  
*on Properties of Low-carbon Medium-chromium Steels of the Air-hardening Type*, 86
- KINEEL, A. B., CRAFTS, W. AND EGAN, J. J.: *Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 169; *Discussion*, 183
- KOSTING, P. R.: *Discussion on Properties of Low-carbon Medium-chromium Steels of the Air-hardening Type*, 86, 87
- KURDJUMOW, G.: *Discussion on Widmanstätten Structure in Iron-carbon Alloys*, 253

## L

- LANDROCK, H. P. *Discussion on An Improved Nickel-chromium Hardened Chilled Cast Iron*, 67
- LESTER, H. H. *Discussion on A New Thermocouple for the Determination of Temperatures up to at Least 1800° C.*, 300
- LORIG, C. H. *Discussion on Precipitation-hardening of Copper Steels*, 165

## M

- MACKENZIE, J. T. *Discussions on Effect of Small Percentages of Chromium on Cast Iron*, 50, 51  
*on An Improved Nickel-chromium Hardened Chilled Cast Iron*, 68 et seq  
*on A New Thermocouple for the Determination of Temperatures up to at Least 1800° C.*, 299  
*on Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 178
- MARTIN, D. J. *Discussion on A New Thermocouple for the Determination of Temperatures up to at Least 1800° C.*, 299
- MARING, G. *Discussion on Homogeneity Limits of Wustite by X-ray Methods*, 285
- MATHEWSON, C. H. *Discussion on Homogeneity Limits of Wustite by X-ray Methods*, 285
- McLAIN, D. *Discussion on Effect of Small Percentages of Chromium on the Quality of Cast Iron*, 49
- MEHL, R. F. *Discussions on Intermediate Phases of the Iron-tungsten System*, 212  
*on Widmanstätten Structure in Iron-carbon Alloys*, 255
- MEHL, R. F., BARRETT, C. S. AND SMITH, D. W. *Studies upon the Widmanstätten Structure, IV.—The Iron-carbon Alloys*, 215
- MUMMA, P. F. AND WRIGHT, E. C. *Properties of Low-carbon Medium-chromium Steels of the Air-hardening Type*, 77

## N

- NORRIS, F. G. *Discussion on Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 182

## P

- PALMER, E. W. AND SMITH, C. S. *The Precipitation-hardening of Copper Steels*, 133
- PAYSON, P. *Discussion on Hot-hardness of High-speed Steels and Related Alloys*, 130
- PFEIL, L. B. *Discussion on Homogeneity Limits of Wustite by X-ray Methods*, 287
- Photomicrographs, care in interpretation necessary, 212
- Pig iron: analyses, effect of coke-ash variations, 28  
 coke-ash variations, effect on analyses, 28

## R

- RAWDON, H. S. *Discussion on Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 180
- RECK, D. L. *Discussion on Oxide Analysis by Iodine Extraction in Steelmaking Problems*, 181
- RUMFORD, L. H. *Discussion on A New Thermocouple for the Determination of Temperatures up to at Least 1800° C.*, 297, 298

## S

- ST. JOHN, A. *Discussions on Homogeneity Limits of Wustite by X-ray Methods*, 286  
*on X-ray Study of Iron-silicon Alloys*, 274
- SAUNDERS, W. M. *Discussion on Effect of Small Percentages of Chromium on the Quality of Cast Iron*, 49
- SAUVEUR, A. *Discussion on Widmanstätten Structure in Iron-carbon Alloys*, 250
- SMITH, C. S. *Discussion on Precipitation-hardening of Copper Steels*, 168
- SMITH, C. S. AND PALMER, E. W. *The Precipitation-hardening of Copper Steels*, 133
- SMITH, D. W., BARRETT, C. S. AND MEHL, R. F. *Studies upon the Widmanstätten Structure, IV.—The Iron-carbon Alloys*, 215
- SMITH, E. K. *Discussion on Effect of Small Percentages of Chromium on Cast Iron*, 50
- SPELLER, F. N. *Discussions on Intermediate Phases of the Iron-tungsten System*, 214  
*on Precipitation-hardening of Copper Steels*, 164 et seq  
*on Properties of Low-carbon Medium-chromium Steels of the Air-hardening Type*, 85, 86
- Steel (See also Iron-carbon Alloys): air-hardening type: low-carbon medium-chromium applications, 77, 85, 86  
 corrosion resistance, 83, 85, 87  
 creep properties, 86, 87  
 physical, properties, 77  
 austenitic: nickel, hot-hardness, experimental study, 98  
 manganese, hot-hardness, experimental study, 98  
 copper: advantages, 164  
 corrosion resistance, 164  
 electrical conductivity, 134  
 precipitation-hardening, 133  
 properties, physical, 138  
 red-shortness, 167  
 rolling characteristics, 165  
 die, hot-hardness, experimental study, 98  
 high-carbon tool, inclusions, electrolytic analysis, with membrane around anode, 185  
 high-speed: cutting efficiency, correlation with hot-hardness, 116, 125, 128  
 hot-hardness: bibliography, 124

- Steel: high-speed: hot hardness, correlation with cutting efficiency, 116, 125, 128  
 experimental study, 98  
 methods of determining, 88  
 nitrided, hot-hardness, 122  
 hot-hardness, experimental study, 88  
 methods of determining, 88  
 inclusions: electrolytic extraction, electrolytes recommended, 186, 193, 194, 196  
 importance, 193  
 in high-carbon tool, electrolytic analysis, with membrane around anode, 185  
 magnetic separation of carbides, 190, 193  
 low-carbon for hot working, hot-hardness, experimental study, 98  
 low-carbon medium-chromium, air-hardening type, applications, 77, 85, 86  
 corrosion resistance, 83, 85, 87  
 creep properties, 86, 87  
 properties, physical, 77  
 nitrided: high-speed, hot-hardness, 122  
 shot samples, difficulty in preparing, 181, 183  
 tool, high-carbon, inclusions, electrolytic analysis, with membrane around anode, 185  
 wood-working, hot-hardness, experimental study, 98
- Steelmaking: iodine method of analysis for steels without the stable carbide-forming elements, 169  
 iodine method for oxide analysis subject to limitations, 181  
 oxide analysis by iodine extraction, for steels without the stable carbide-forming elements, 169  
 processes, trends in tonnage, 13  
 brief description, 13
- Stellite: hot-hardness: experimental study, 98, 114, 126  
 methods of determining, 95
- STOUGHTON, B.: *Discussion on An Improved Nickel-chromium Hardened Chilled Cast Iron*, 75
- STYRI, H.: *Analyses of Inclusions in High-carbon Tool Steels*, 185; *Discussion*, 193, 196
- STYRI, H.: *Discussion on Properties of Low-carbon Medium-chromium Steels of the Air-hardening Type*, 86
- Surfacing metals. See Hard-coating Alloys.
- SYKES, W. P. AND VAN HORN, K. R.: *The Intermediate Phases of the Iron-tungsten System*, 198; *Discussion*, 213, 214
- T
- Thermocouple: carbon-silicon carbide, for determination of temperatures up to at least 1800° C., 290
- V
- VAN HORN, K. R. AND SYKES, W. P. *The Intermediate Phases of the Iron-tungsten System*, 198
- VANICK, J. S.: *An Improved Nickel-chromium Hardened Chilled Cast Iron*, 53, *Discussion*, 68 et seq  
*Discussion on Effect of Small Percentages of Chromium on Cast Iron*, 50
- W
- WATERHOUSE, G. B. *Steelmaking Processes*, 13
- WEAVER, F. I. *Discussion on Effect of Small Percentages of Chromium on Cast Iron*, 50
- Widmanstätten figures: discovery in metals, 250  
 scope of term, 252  
 structure See Iron-carbon Alloys
- WILMOT, G. S.: *Discussion on An Improved Nickel-chromium Hardened Chilled Cast Iron*, 66
- WISSLER, W. A. AND DAY, R. O. *Discussion on Hot-hardness of High-speed Steels and Related Alloys*, 125
- WRIGHT, E. C. *Discussion on Properties of Low-carbon Medium-chromium Steels of the Air-hardening Type*, 86, 87
- WRIGHT, E. C. AND MUMMA, P. F.: *Properties of Low-carbon Medium-chromium Steels of the Air-hardening Type*, 77
- Wüstite, homogeneity limits, X-ray study 176













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